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Ozonation of a Municipal Groundwater
Supply to Reduce Iron and Manganese

By

Steven Lance Schjodt

OZONATION OF A MUNICIPAL GROUNDWATER
SUPPLY TO REDUCE IRON AND MANGANESE

BY

STEVEN LANCE SCHJODT

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Civil Engineering, South Dakota
State University

1983

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OZONATION OF A MUNICIPAL GROUNDWATER
SUPPLY TO REDUCE IRON AND MANGANESE

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Dr. Dwayne A. Rottag
Thesis Adviser and
Head of Major Department

Date

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
LITERATURE REVIEW	4
METHODS AND MATERIALS	8
Description of Pilot Plant	8
Experimental Procedures	13
Generator Calibration	13
Pilot Plant Operation	16
Transfer Efficiency	20
Temperature and pH	22
Chlorine Demand	22
Iron and Manganese	23
Filter Head Loss	26
RESULTS AND DISCUSSION	27
Transfer Efficiency	27
Ozone Dosage Effects	27
Detention Time Effects	29
Ozone Demand	29
Temperature and pH	30
Temperature	30
pH	30
Iron and Manganese	33
Contact Columns Effluent	33

Filter Effluent	38
Filter Performance	40
Filter Head Loss	42
Chlorine Demand	46
Cost of Ozonation	50
CONCLUSIONS	55
RECOMMENDATIONS FOR FUTURE STUDIES	57
LITERATURE CITED	58
APPENDIXES	
Appendix A. List of Symbols and Abbreviations	60
Appendix B. Experimental Calculations	62
Appendix C. Transfer Efficiency and Ozone Residual: Results and Statistical Analyses	66
Appendix D. Raw Water Samples: Temperature, pH, Chlorine Demand, and Iron and Manganese Concentrations	69
Appendix E. Hydrogen Ion Concentrations: Results and Statistical Analyses	71
Appendix F. Iron and Manganese: Results and Statistical Analyses	74
Appendix G. Filter Head Loss: Results	85
Appendix H. Chlorine Demand: Results and Statistical Analyses	87
Appendix I. Description of the Treatment Process at the Sioux Falls Water Treatment Plant	89
Appendix J. Ozonation Cost Calculations	93

LIST OF TABLES

Table	Page
1. Liquid Flow Rates and Ozone Concentrations Associated with Various Combinations of Ozone Dosage and Detention Time	19
2. Cost of Constructing and Operating an Ozonation System . .	52
3. Total Annual Cost of Ozonation at Various Interest Rates .	54
C1. Transfer Efficiencies (per cent)	67
C2. Analysis of Variance of Transfer Efficiency Data	67
C3. Ozone Residuals (mg O ₃ /l H ₂ O)	68
C4. Analysis of Variance of Ozone Residual Data	68
E1. Hydrogen Ion Concentrations in CC-2 Effluent (H ⁺ X 10 ¹⁰) .	72
E2. Analysis of Variance of CC-2 Effluent Hydrogen Ion Concentrations	72
E3. Hydrogen Ion Concentrations in Filter Effluent (H ⁺ X 10 ¹⁰)	73
E4. Analysis of Variance of Filter Effluent Hydrogen Ion Concentrations	73
F1. Soluble Iron in CC-2 Effluent (mg/l)	75
F2. Analysis of Variance of CC-2 Effluent Soluble Iron Concentrations	75
F3. Soluble Manganese in CC-2 Effluent (mg/l)	76
F4. Analysis of Variance of CC-2 Effluent Soluble Manganese Concentrations	76
F5. Soluble Iron in Filter Effluent (mg/l)	77
F6. Analysis of Variance of Filter Effluent Soluble Iron Concentrations	77
F7. Total Iron in Filter Effluent (mg/l)	78

F8.	Analysis of Variance of Filter Effluent Total Iron Concentrations	78
F9.	Soluble Manganese in Filter Effluent (mg/l)	79
F10.	Analysis of Variance of Filter Effluent Soluble Manganese Concentrations	79
F11.	Total Manganese in Filter Effluent (mg/l)	80
F12.	Analysis of Variance of Filter Effluent Total Manganese Concentrations	80
F13.	Iron and Manganese Concentrations in Filter Influent as a Function of Time (mg/l)	81
F14.	Iron and Manganese Concentrations in Filter Effluent as a Function of Time (mg/l)	82
F15.	Iron Removal Profiles Through Filter Medium	83
F16.	Manganese Removal Profile Through Filter Medium	84
G1.	Head Loss Through Filter Medium	86
H1.	Chlorine Demand of Pilot Plant Effluent (mg/l)	88
H2.	Analysis of Variance of Pilot Plant Effluent Chlorine Demand	88
J1.	Computation of Cost-Updating Indices	94
J2.	Computation of Costs of Ozonation	95

LIST OF FIGURES

Figure	Page
1. Ozone Generation System	9
2. Schematic Diagram of Ozone Generation System	10
3. Schematic Diagram of Contact Columns	12
4. Sectional View of Pilot Filter	14
5. Sampling Diagram	21
6. Transfer Efficiency Versus Ozone Dosage	28
7. Ozone Residual Versus Ozone Dosage	28
8. Contact Column Two Effluent pH Versus Ozone Dosage	32
9. Filter Effluent pH Versus Ozone Dosage	32
10. Water pH Versus Sampling Location	34
11. Soluble Iron in CC-2 Effluent Versus Ozone Dosage	35
12. Soluble Manganese in CC-2 Effluent Versus Ozone Dosage	35
13. Iron Concentrations in the Filter Effluent Versus Time Since Backwash	41
14. Manganese Concentrations in the Filter Effluent Versus Time Since Backwash	41
15. Iron Removal Profile Through Filter Medium (15 Minutes after Backwash)	43
16. Manganese Removal Profile Through Filter Medium (15 Minutes after Backwash)	43
17. Iron Removal Profile Through Filter Medium (16 Hours after Backwash)	44
18. Manganese Removal Profile Through Filter Medium (16 Hours after Backwash)	44
19. Iron Removal Profile Through Filter Medium (32 Hours after Backwash)	45

20.	Manganese Removal Profile Through Filter Medium (32 Hours after Backwash)	45
21.	Head Loss Through Filter Medium	47
22.	Filter Head Loss Versus Volume of Water Filtered	48
11.	Sioux Falls Water Treatment Plant Flow Diagram	91

INTRODUCTION

Both iron and manganese are present in insoluble forms in significant amounts of nearly all soils. Iron exists in soils and minerals mainly as insoluble ferric oxide (Fe_2O_3) and iron sulfide (FeS_2) while manganese exists primarily in the soil as insoluble manganese dioxide (MnO_2) (15).

Groundwaters often contain considerable amounts of carbon dioxide and under anaerobic conditions, the ferric and manganic compounds are reduced by the slightly acidic water to their soluble ferrous and manganous states, and solution occurs without difficulty (8) (12) (15). The development of anaerobic conditions is essential for appreciable amounts of iron and manganese to gain entrance to a water supply. For this reason, groundwaters usually contain much higher concentrations of iron and manganese than do surface waters (15).

An oxidation process is the best method for removing soluble iron and manganese. During an oxidation process, the soluble ferrous (Fe^{+2}) and manganous (Mn^{+2}) compounds will be converted to ferric (Fe^{+3}) and manganic (Mn^{+4}) precipitates such as ferric hydroxide ($\text{Fe}(\text{OH})_3$) and MnO_2 (15).

Humans suffer no known harmful effects from drinking waters containing iron and manganese. However, for economic and aesthetic reasons, the 1962 water quality standards established by the United States Public Health Service (USPHS) recommended maximum iron and

manganese concentrations of 0.3 and 0.05 mg/l respectively (13). Furthermore, the goal of the American Water Works Association (AWWA) is to maintain levels of iron and manganese below 0.05 and 0.01 mg/l respectively (3).

Iron and manganese concentrations in excess of the USPHS limits are objectionable for the following reasons (1) (2) (3) (15) (17):

1. The precipitation of iron and manganese alters the appearance of water, turning it a yellow-brown to black.
2. Iron and manganese precipitates cause black and brown stains on laundry and porcelain plumbing fixtures.
3. Clonothrix and Crenothrix, which are commonly called iron bacteria, use iron and manganese in their metabolism. If small amounts (0.1 mg/l) of iron and manganese are allowed to enter the distribution system, these forms of life may thrive and cause slimes which will, in turn, reduce the effective area of distribution pipes, clog meters, and obstruct valves.
4. When the bacterial growths die off and decay, taste and odor problems occur.
5. Increased flow rates frequently resuspend iron and manganese deposits, resulting in high turbidities.
6. Iron- and manganese-bearing waters may impart a disagreeable color or taste to beverages as well as forming a dark deposit on vegetables during cooking.
7. Water containing iron and manganese is unsuitable for many industrial processes including paper manufacturing, dyeing, bleaching, and film developing.
8. Iron and manganese themselves, in concentrations greater than a few milligrams per liter, will impart a metallic or bitter taste to the water.

The city of Sioux Falls, South Dakota obtains its water supply from the Big Sioux aquifer below and adjacent to the Big Sioux River north of Sioux Falls. While there are two surface supply intakes on

the diversion canal, the city mainly depends on a field of 34 wells to provide the water needed. Because the raw water generally has iron concentrations in the range of 3.0 to 6.0 mg/l and manganese concentrations in the range of 2.0 to 2.6 mg/l, the treatment process is designed primarily to remove iron and manganese. The city presently employs prechlorination, lime softening, flocculation, recarbonation, chlorination, fluoridation, and filtration. Iron and manganese levels in the finished water comply with the USPHS recommended standards. A detailed description of the treatment process is provided in Appendix I.

The purpose of this study was to determine the feasibility of using ozonation followed by filtration to remove iron and manganese. A small scale pilot plant was utilized to generate and expose the ozone to the raw water. The filter media and filtering rates employed during the pilot studies were identical to those used at the Sioux Falls Water Treatment Plant.

LITERATURE REVIEW

Ozone is a very effective disinfectant for drinking water supplies. Based upon a comprehensive review of the literature, Stoebner (17) pointed out a number of advantages and disadvantages of treating groundwater with ozone.

As an alternative disinfectant for a groundwater supply, ozone has six distinct advantages:

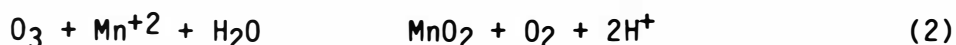
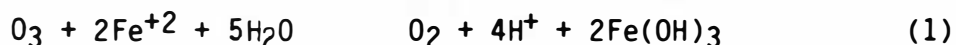
1. Ozone precipitates iron and manganese.
2. Ozone reduces the potential for trihalomethane formation.
3. Ozone reduces the chlorine demand of water.
4. Ozone is unsurpassed for destroying bacteria, viruses, pathogens, and spores.
5. Ozone effectively reduces taste, odor, and color.
6. Ozone destroys organic pollutants including pesticides.

As an alternative disinfectant for a groundwater supply, there are four factors associated with ozone that may be considered disadvantages:

1. Ozone does not provide a lasting residual to guard against recontamination in the distribution system.
2. Ozone decomposes very rapidly making long contact time between the water and the disinfectant difficult to achieve.
3. Ozone must be produced on site and relatively elaborate generating equipment is required.
4. Ozonation generally has a higher total cost than does chlorination.

Ozone will react with reduced metals and organic material in groundwater. Since the amount of organic matter in the Sioux Falls

groundwater is relatively small, the primary ozone demand is exerted by the iron and manganese. Considering the iron and manganese in the water, the following equations represent the reaction of ozone with the metals under near-neutral conditions (10):



These equations indicate that 0.43 mg/l of ozone would react with one mg/l iron, and 0.87 mg/l ozone would react with one mg/l manganese. Based on the waters containing 4.0 mg/l of iron and 2.3 mg/l manganese, and no excess of ozone, the theoretical ozone requirement would be:

$$4.0 \text{ mg/l} \times 0.43 = 1.72 \text{ mg/l}$$

$$2.3 \text{ mg/l} \times 0.87 = 2.00 \text{ mg/l}$$

$$\underline{3.72 \text{ mg/l}}$$

Other constituents in the water, such as sulfides, bacteria, and organics will also exert an additional ozone demand. However, this demand is expected to be much lower than the combined iron and manganese demand. In addition, an excess of ozone is required under neutral conditions to provide enough force to drive the reactions to completion. Thus, the actual ozone demand will exceed 3.72 mg/l.

In 1980 Kirk (10) provided a comprehensive account of a pilot plant study conducted at the city of New Ulm, Minnesota to determine the ozone dosage necessary to reduce the iron and manganese content of the water to within acceptable limits. The raw water contained 0.4 mg/l iron and 1.5 mg/l manganese.

The pilot plant was sized to treat a 1 gpm sidestream of the raw water being treated at the filter plant. The pilot plant consisted of a laboratory model ozone generator, a glass column contacting unit, and a filter unit. The filter contained 12 inches of graded gravel, 22 inches of sand, and 8 inches of anthrafilt.

Ozone concentrations in the air stream admitted to the contact unit were varied at periodic intervals by changing the power setting on the generator. Water samples were taken daily and shipped to a private laboratory for analysis.

Kirk found that treating the raw water with 2.6 mg/l ozone, using a contact time of nine minutes, removed the iron and manganese to below the USPHS standards. Filtration studies indicated that the above gradation functioned satisfactorily to remove colloidal manganese and iron. Also, a filtration rate of 2 gpm/ft² was found to be adequate.

Since ozonation oxidizes organic matter and precipitates iron and manganese, ozone treatment of water should reduce the chlorine demand of the water. In New Ulm, as a result of ozonation, Kirk (10) concluded that no appreciable chlorine demand was exerted by the treated water, and therefore, chlorine applications sufficient to maintain a residual was all that was required.

Furgason and Day (6) published a comparison of the costs of various treatment systems for removing iron and manganese. The methods included ozonation, ion exchange, chemical oxidation with

gravity filtration, chemical oxidation with pressure filtration, and contact filtration using manganese greensand. The results showed that although the capital investment for ozone exceeded other systems, the operating cost was low, thus making the annual cost competitive.

METHODS AND MATERIALS

Description of Pilot Plant

The basic components of the pilot plant used in this study were an ozone generation system, two contact columns, a constant-head tank, and an anthracite filter. The generation system is illustrated in Figure 1. The generation system included a power supply, an air preparation system, and the generator itself. The ozone generation system and the contact columns were supplied by Emery Industries, Inc., Cincinnati, Ohio and have been described in detail by DeBoer (4) and Stoeber (17). The filter was the same as that used by Quail (14) and the filter media was taken from the filters at the Sioux Falls Water Treatment Plant to ensure the use of ripened media.

A schematic diagram of the generation system is presented in Figure 2. As shown in the schematic, atmospheric air was first filtered and compressed to a pressure of 690 kPa (100 psig). The compressed air was then cooled and stored in a pressure tank. Next, oil, moisture, and dust were removed from the air by passing it consecutively through a pre-filter, to remove any oil in the air introduced by the compressor, the desiccator, and the after-filter to remove any desiccant dust. Prior to entering the generator, the air pressure was reduced from 690 kPa (100 psig) to 100 kPa (15 psig) by a pressure regulator.

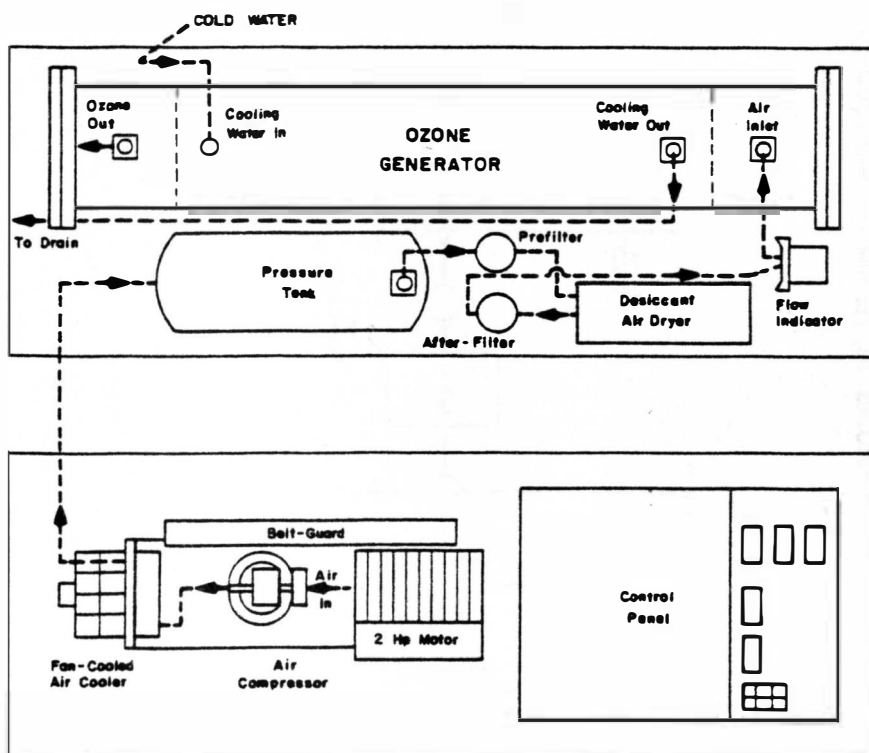


Figure 1. Ozone Generation System

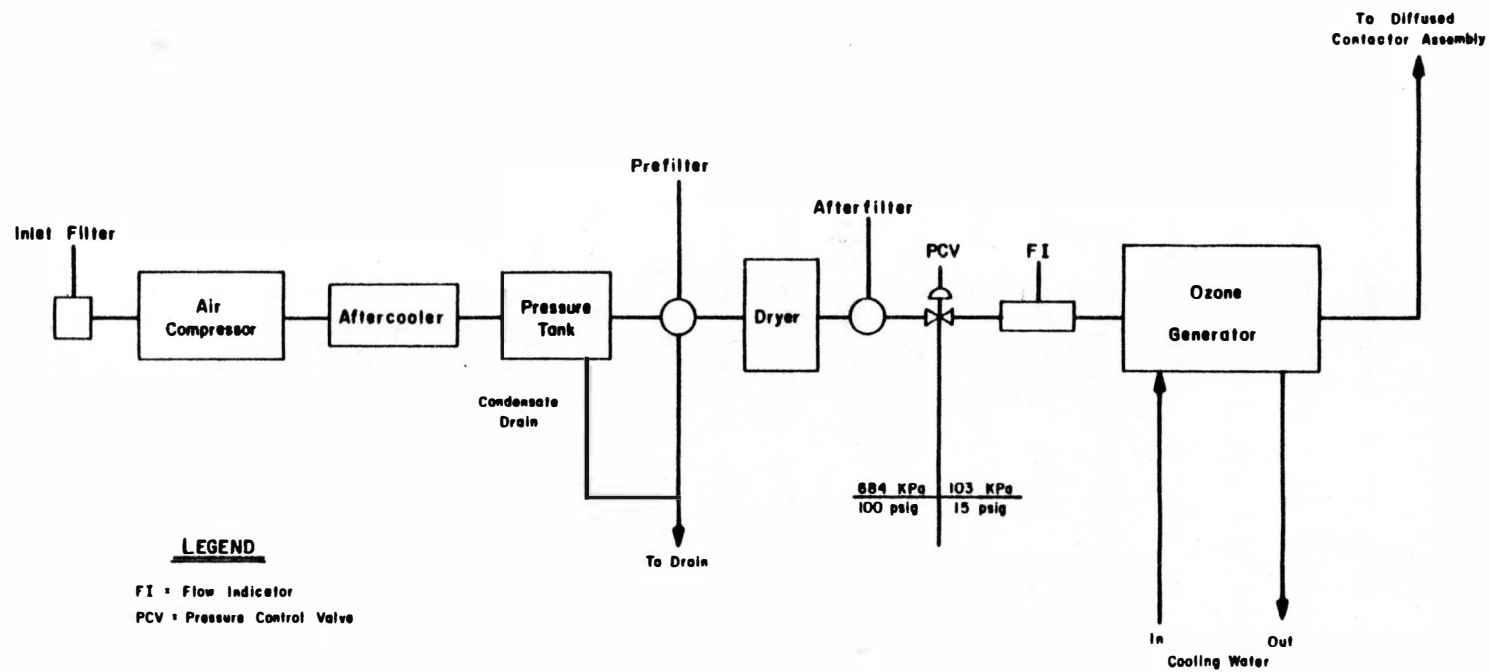


Figure 2. Schematic Diagram of Ozone Generation System

The basic components of the ozone generator were three stainless steel tubes enclosed within a single compressed air module. Tubular glass dielectrics were centered inside each steel tube and a stainless steel grid, which served as the high-voltage electrode, was inserted into each glass tube. Clean, dry air passed through the annular air space between the outside of the glass tube and the stainless steel shell. The corona, which discharged across the air space, caused a small percentage of the oxygen in the feed gas to be converted to ozone. Water was circulated around the exterior of the steel tubes to dissipate the heat from the corona. The ozonized air from the generator was routed to the contact columns.

The two contact columns are shown schematically in Figure 3. Each stainless steel column had an inside diameter of 15.2 cm (6 in) and a total height of 4.88 m (16 ft). The ozone-rich gas entered the bottom of the columns through porous stainless steel diffusers. Flow of the ozone-rich gas to each diffuser was regulated with a ball valve and a rotameter at the base of each column. Raw water was pumped to the top of the first column by a variable-speed positive-displacement pump. The arrangement of the columns allowed water and ozone to flow counter-currently in both columns. Upon leaving the bottom of the second column, the ozonized water flowed to a constant-head tank located above the filter.

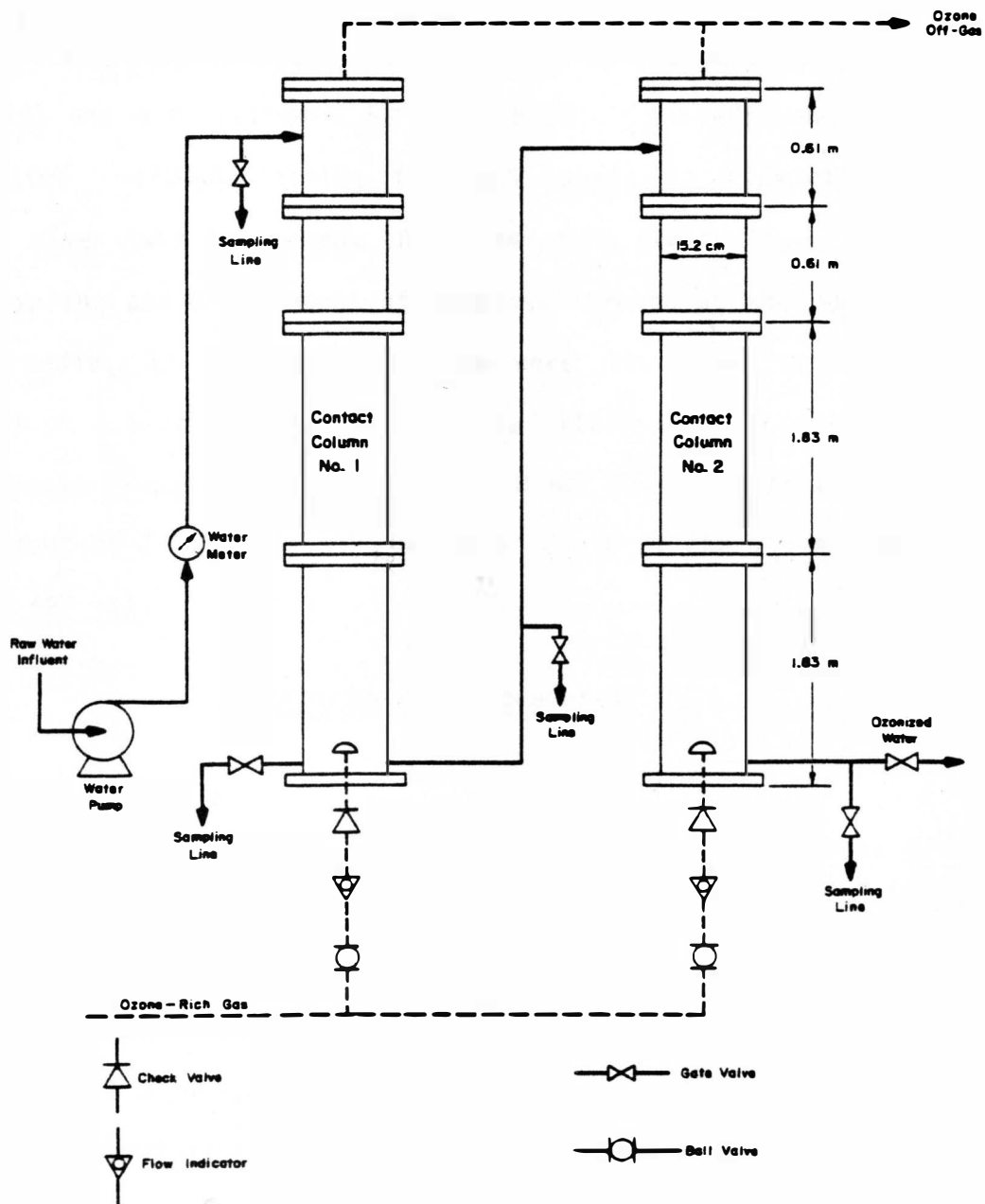


Figure 3. Schematic Diagram of Contact Columns

The sole purpose of the constant-head tank was to allow a constant flow of water into the filter. The pilot filter, shown in Figure 4, was made of transparent PVC with an inside diameter of 15.2 cm (6 in) and a height of 2.51 m (8.25 ft). The effluent line from the filter included valving for backwashing, a flowmeter, and a plastic riser tube to prevent the filter from dewatering. To facilitate sampling and measurement of headloss throughout the depth of the filter media, 12 piezometric tubes were installed in the filter sidewall on 7.5-cm (3-in) centers. The filter media consisted of No. 1 anthracite ranging from 0.6 to 0.8 mm in size with a uniformity coefficient of 1.75 or less. The total depth of the filter media was 68.6 cm (27 in).

Experimental Procedures

Generator Calibration

Ozone production depends upon the dryness and flow rate of the feed gas; the temperature and pressure in the ozone generator; and the frequency and voltage of the power supply. All of these parameters were held constant except voltage. The feed-gas flow-rate was held constant at 11 slpm (0.39 scfm), the ozone generator was maintained at constant temperature of 10°C (50°F) and pressure of 100 KPa (15 psig), and the frequency was a uniform 60 Hz. In this manner, the ozone production became a function of the voltage only and calibration of the generator was simply a matter of determining the concentration of

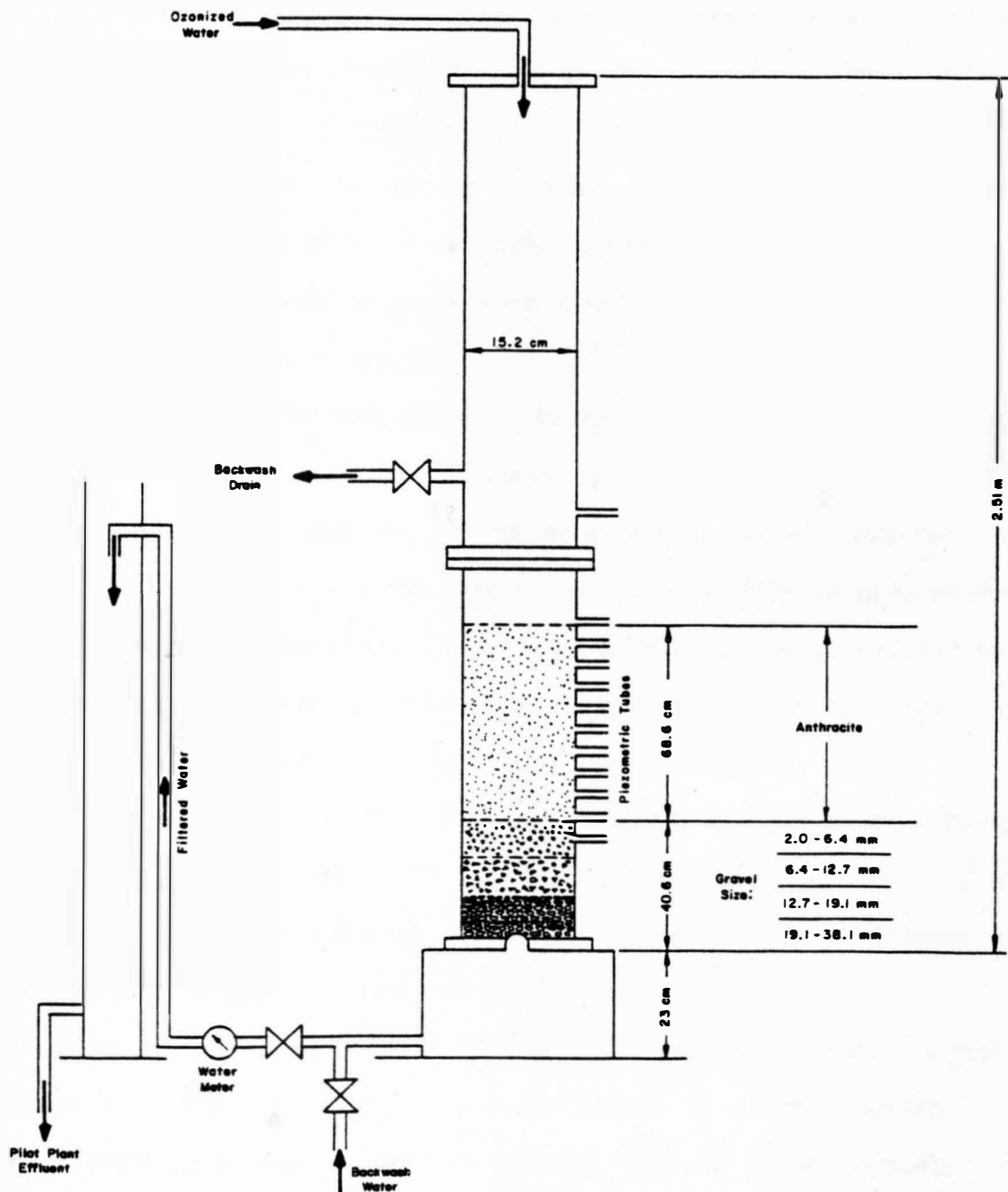


Figure 4. Sectional View of Pilot Filter

ozone in the air leaving the generator at a number of different voltages.

The method used to determine the ozone concentration in the gas is a variation of the iodometric method for measuring ozone residual described in Standard Methods (16). In brief, a small 4-liter portion of supply gas was passed through a series of two gas washing bottles, each containing 400 ml of 1 per cent potassium iodide (KI) solution. The volume of gas was measured with a wet-test meter. The ozone in the supply gas became entrapped in the KI solution and subsequent titration with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) yielded the exact weight of ozone in the KI solution. By knowing the air volume that passed through the bottles and the weight of ozone in the KI solution, the concentration of ozone in the supply gas could readily be determined.

The ozone production of the generator could be calculated from the air flow rate and concentration of ozone in the air. A description of the calculations is given in Appendix B.

The generator calibration curve obtained in this experiment was nearly the same as that obtained by Stoebner (17) and used in his experiment. At low and high voltages, a large change in voltage was necessary to produce a small change in ozone concentration. In the mid-voltage range, 60 to 70 per cent of maximum voltage, a small change in voltage resulted in a large change in ozone concentration. The relationship between applied voltage into the ozone generator and ozone concentration in the supply gas was nonlinear. Thus, doubling

the power input to the ozone generator did not necessarily double the ozone production.

A problem was encountered with the air-drying system during the course of this experiment. The dual-tower desiccant air dryer was designed to dry the feed gas down to a dewpoint of -40°F . However, numerous checks with a dewpoint indicator revealed that the actual dewpoint of the feed gas was in the range of 0 to -10°F . This caused the ozone generation system to operate at less than peak energy efficiency and also introduced the possibility of corrosive conditions at the electrode from the reaction of nitrogen and moisture in the feed gas to form nitric acid. Fortunately, the energy efficiency of the pilot plant was not pertinent to the results of this investigation.

A flaw in the basic design of the dual-tower desiccant air dryer was later determined to be the cause of the moisture problem in the feed gas. It was discovered that while one tower was absorbing moisture the other tower was not purging properly.

Pilot Plant Operation

The independent variables in this investigation were ozone dosage and detention time. All other parameters were held constant. Research conducted earlier by DeBoer (4) had revealed that the most efficient use of ozone occurred when: 1) the liquid depth in the contact columns was 4.4 m (14.5 ft); 2) the water and supply gas were flowing counter-currently in both columns; and 3) the supply gas was proportioned so that 60 per cent flowed to the first column and 40 per

cent flowed to the second column. Consequently, this configuration and proportionment were adopted for use throughout this investigation.

Stoebner (17) has provided a detailed description of the pilot plant operation in his thesis. Basically, detention time was a function of liquid volume and water flow rate in the contact columns, and since liquid volume was held constant, detention time became a function of water flow rate only. The influent water flow rate was controlled by a positive-displacement pump with a variable-speed DC motor. The water flow rate could be varied from 3.8 lpm to 41.6 lpm (1 gpm to 11 gpm). Since the contact columns had a constant liquid volume of 161 liters (42.6 gallons), detention times of 5 to 45 minutes were readily obtainable.

Applied ozone dosage was a function of ozone concentration in the supply gas, supply gas flow rate, and water flow rate. However, since the supply gas flow rate was held constant, the applied ozone dosage was actually a function of the generator power input and the water flow rate only.

The following expression was obtainable for ozone concentration in the generator off-gas.

$$C_i = DV/TQ_g \quad (3)$$

where:

C_i = ozone concentration in the generator off-gas (mg/l)

D = applied ozone dosage (mg/l)

V = liquid volume of contact columns (liters)

T = liquid detention time (minutes)

Q_g = gas flow rate (slpm)

However, since V was held constant at 161 liters and Q_g was held constant at 11 slpm, C_i could be expressed as a constant times the ratio of applied ozone dosage to detention time:

$$C_i = 14.65 D/T \quad (4)$$

With this simple expression, given any combination of ozone dosage and detention time, the required ozone concentration in the off-gas could be calculated. The required voltage setting on the ozone generator could then be determined from the calibration curve.

Based upon theoretical ozone requirements of the Sioux Falls well water, the required ozone dosage was estimated to be about 4 mg/l. Therefore, it was decided that ozone dosages between 2 and 12 mg/l should be studied. Detention time effects were studied between 5 and 30 minutes.

Table 1 lists the water flow rate (Q_1) and C_i values associated with the various combinations of ozone dosage and detention time. Under the particular operating conditions in this investigation, the ozone generator was not capable of producing more than 14 mg/l ozone using all three tubes. Consequently, certain combinations involving high ozone dosages and short detention times were not obtainable. Therefore, of the five ozone dosages and five detention times shown in Table 1, only 22 of the 25 possible operating modes were feasible.

Table 1. Liquid Flow Rates and Ozone Concentrations Associated with Various Combinations of Ozone Dosage and Detention Time

Detention Time (minutes)		5	10	15	20	30
Q_1 (lpm)		34.0	17.0	11.33	8.50	5.67
Applied Ozone Dosage (mg/l)	0	0.0 0%	0.0 0%	0.0 0%	0.0 0%	0.0 0%
	2	5.9 70%	2.9 62%	2.0 60%	1.5 58%	1.0 56%
	4	11.7 94%	5.9 70%	3.9 65%	2.9 62%	2.0 60%
	8	23.4 *	11.7 94%	7.8 77%	5.9 70%	3.9 65%
	12	35.2 *	17.6 *	11.7 94%	8.8 82%	5.9 70%

Legend:

C_1 = ozone concentration in ozonized air, mg/l

% = per cent of max ozone generator voltage

$C_1 = 14.65 \text{ D/T}$

* above the maximum ozone generator output

These 22 combinations of ozone dosage and detention time were used as the basis for the transfer efficiency, temperature, pH, chlorine demand, and iron and manganese investigations.

Transfer Efficiency

It was of interest, during the course of the investigation, to study the effect of ozone dosage and detention time on ozone transfer efficiency. Ozone transfer efficiency was defined as follows:

$$E = 100 (W_i - W_o) / W_i \quad (5)$$

where:

E = transfer efficiency (per cent)

W_i = weight of ozone entering the contact columns (g/hr)

W_o = weight of ozone leaving the contact columns (g/hr)

To determine the transfer efficiency at each of the operating runs, it was necessary to collect gas samples at the two locations shown in Figure 5. The procedure used to analyze each of the gas samples was the same as that described earlier.

Ozone residual and its influence on transfer efficiency was also investigated. Therefore, ozone residual was monitored at each of the operating runs. The method used to analyze ozone residuals was the iodimetric method described in Standard Methods (16). Ozone was first purged from an 800-ml water sample by passing a stream of nitrogen through the sample at a rate of 1.0 l/m for approximately 5 minutes. The liberated ozone was then absorbed in 400 ml of potassium iodide (KI) and subsequent titration with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$)

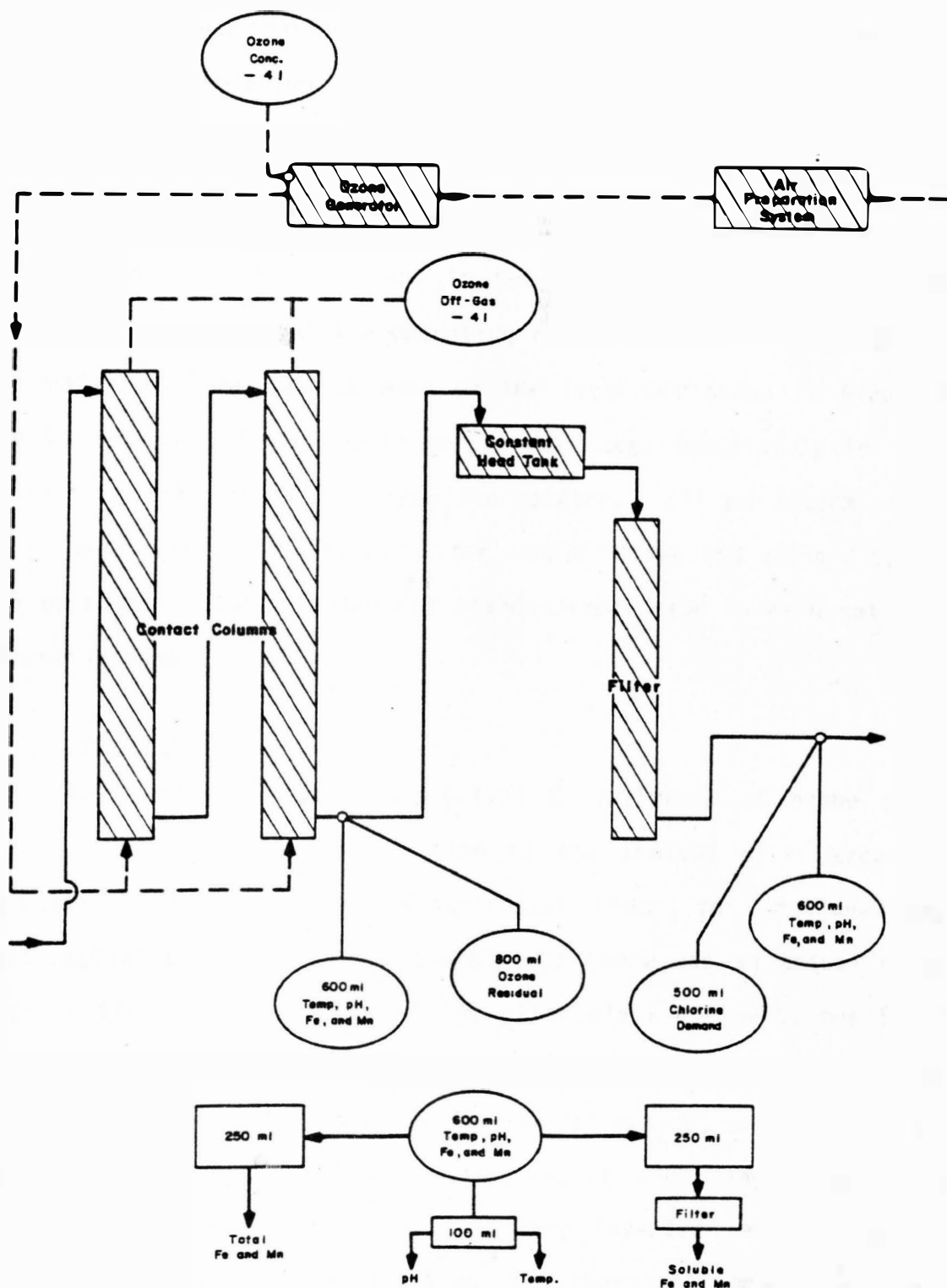


Figure 5. Sampling Diagram

yielded the concentration of ozone residual in the water. A description of the calculations involved is included in Appendix B.

Temperature and pH

The temperature and pH of water usually have an influence upon the rate of chemical reactions in the water treatment process. For this reason, at each of the operating runs, the temperature and pH of the water was measured at each of the locations shown in Figure 5. The temperature of each water sample was taken immediately following collection using a mercury-type thermometer. All pH determinations were made within 15 minutes after sample collection using a Corning 125 pH meter. The pH meter was standardized prior to each set of pH determinations.

Chlorine Demand

The oxidation and disinfection capabilities of ozone should preclude the need for chlorination of the treated water except to maintain a residual in the distribution system for continued bacteriological protection. To determine if there was an actual reduction in the chlorine demand of the pilot plant effluent, one 500-ml sample of filter effluent was collected during each pilot plant operating run. Immediately following collection, each sample was dosed with 8.5 mg/l chlorine (equivalent to the dosage used in the treatment process). The sample was then inverted several times to ensure that the chlorine solution was thoroughly mixed, and then

stored in a dark location for 30 minutes. After 30 minutes expired, the chlorine residual was measured by the amperometric method as described in Standard Methods (16). A Fisher 397 Chlorine Titrimeter was used to measure both free and total chlorine residual. The approximate chlorine demand was then determined by subtracting the chlorine residual from the 8.5 mg/l dose. The calculations involved in determining chlorine demand are outlined in Appendix B.

Iron and Manganese

The primary objective of this investigation was to study the effects of the ozonation/filtration process on iron and manganese removal. It was necessary to determine whether the process could reduce the iron and manganese concentrations in the Sioux Falls groundwater to levels below the USPHS drinking water standards. Furthermore, it was necessary to determine the economical operating conditions, i.e. the combination of ozone dosage and detention time which would most economically reduce the iron and manganese to acceptable levels.

The filtration rate used during this study was 5 meters/hour (2 gpm/ft²). This filtration rate was in accordance with the design specifications of the filters employed at the Sioux Falls Water Treatment Plant. The filter media was obtained from one of the operating filters in the treatment plant and as a result, no ripening period was necessary. Except for the optimum operating run, to be described later, the filter was backwashed every 20 hours of

operation. The filter was backwashed until the backwash water was clear (usually about 10 to 15 minutes) at a rate of about 37 meters/hour (15 gpm/ft²).

At each of the 66 operating runs, a 600-ml raw water sample was collected, and two 600-ml samples were collected at the locations shown in Figure 5. Each of these samples were then analyzed for temperature, pH, and iron and manganese concentrations as shown at the bottom of Figure 5.

Once an optimum dosage and detention time was established, an additional "filter run" was conducted at that dosage and detention time to determine the maximum practical length of filter run. The filter was backwashed prior to the start of the filter run, and filtration continued until breakthrough occurred. During this optimum run, filter influent and effluent samples were collected every 30 minutes during the first hour, every hour during the next three hours, and then every four hours until filter breakthrough. These samples were then analyzed for iron and manganese concentrations to determine if the quality of the filter influent and filter effluent varied with time. Also, at 16-hour intervals beginning immediately after filter backwash, the filter profile was sampled. This was accomplished by sampling each of the nine piezometric tubes in the filter sidewall that encompassed the depth of the media. These samples were also analyzed for iron and manganese concentrations in order to examine the

"removal profile" of the filter media and to determine whether it changed with time.

In order to analyze for soluble iron and manganese, a portion of each water sample had to be filtered with a 0.45-micron membrane filter. This was accomplished with the aid of a vacuum pump apparatus. Each sample was stored in a plastic bottle and preserved with the addition of 2 ml concentrated hydrochloric acid (HCl) which lowered the pH to below 2.0. The portion of each sample that was analyzed for total iron and manganese was not filtered but placed directly in a plastic bottle and preserved with HCl.

Those samples with iron concentrations below 0.5 mg/l and/or manganese concentrations below 0.3 mg/l needed to be concentrated prior to analysis. The samples were concentrated by first evaporating a 100 ml portion of sample to dryness on a steam table. The residue was then redissolved using 2 ml of 1:1 HCl. The solution was then transferred to a 10-ml volumetric flask, and then the dish was rinsed with approximately 3 ml of demineralized water. Next, the acidic solution was neutralized with 1 ml of 1:1 ammonium hydroxide (NH₄OH). Finally, the sample was brought to a volume of 10 ml using demineralized water.

A Perkin-Elmer 503 Atomic Absorption Spectrophotometer, with a digital absorbance output, was used to analyze for iron and manganese. Standards of 5.0, 2.5, 1.0, 0.5, and 0.1 mg/l were prepared from a stock solution in accordance with Standard Methods (16). A linear

relationship existed between concentration and relative absorbance of the standard curve. For each standard and sample, the instrument read and displayed an average of three consecutive absorbance determinations. This was done three times, so in effect, an average of nine absorbance values was recorded for each standard and sample.

Filter Head Loss

In this part of the investigation, filter head loss as a function of both media depth and volume of water filtered was evaluated. Head loss data were recorded during the special filter run described previously. The water levels in each of the twelve piezometric tubes were recorded at 4-hour intervals. The difference in water level between any two adjacent piezometric tubes represented the head loss through that particular 7.6-cm (3-in) segment of filter media. Consequently, the total head loss was the difference in water levels between the first piezometric tube and the discharge level of the effluent riser.

RESULTS AND DISCUSSION

Transfer Efficiency

Ozone Dosage Effects

The transfer efficiency data are illustrated in Figure 6 and tabulated in Table C1. In Figure 6, the mean transfer efficiencies for the five detention times are plotted as functions of ozone dosage. Apparently, at any given detention time, the transfer efficiency decreased with increased ozone dosage. An analysis of variance of the data, shown in Table C2, confirmed that a highly significant difference (1 per cent level) existed between the mean transfer efficiencies at the various ozone dosages. A decrease in transfer efficiency with increased ozone dosage was also observed by DeBoer (4) and Stoebner (17) in their investigation of transfer efficiency. At higher ozone dosages, a greater portion of the ozone demand is apparently being satisfied and the remaining ozone is being released as off-gas. This hypothesis can be supported by noting the strong correlation that exists between ozone residual and applied ozone dosage in Figure 7. This correlation indicates that, at higher ozone dosages, the demand is either being satisfied or exceeded.

From Figure 7 it can be observed that the ozone residual increased with increases in ozone dosage above 4 mg/l, with the increases being more pronounced at the shorter detention times. At the 4 mg/l dosage level and lower, all the ozone was consumed and no

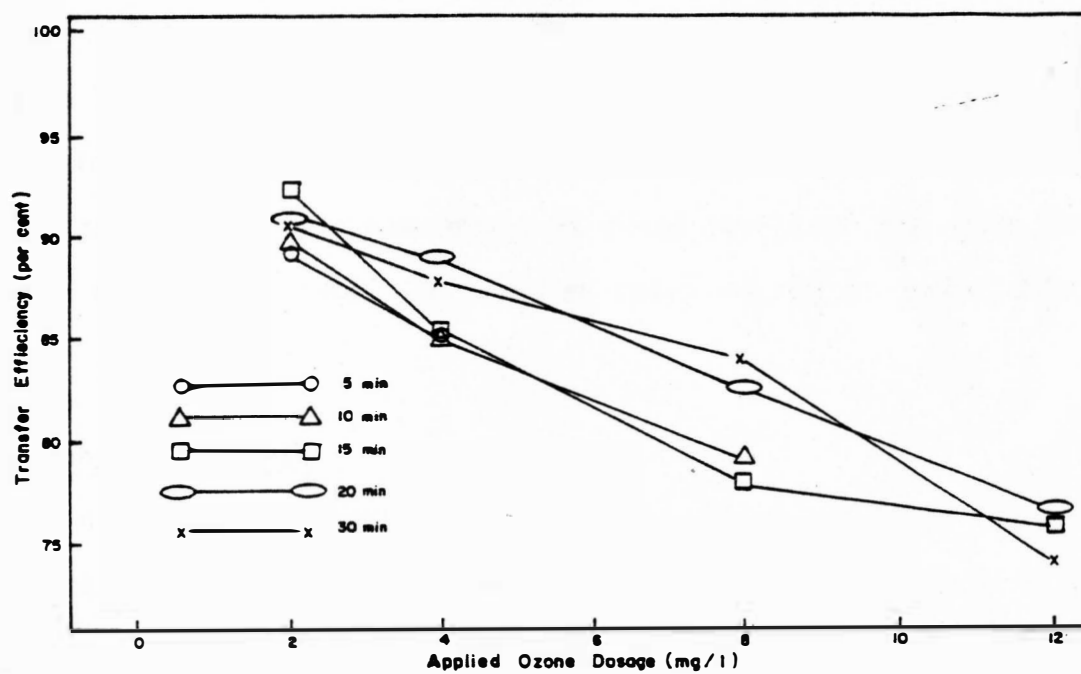


Figure 6. Transfer Efficiency Versus Ozone Dosage

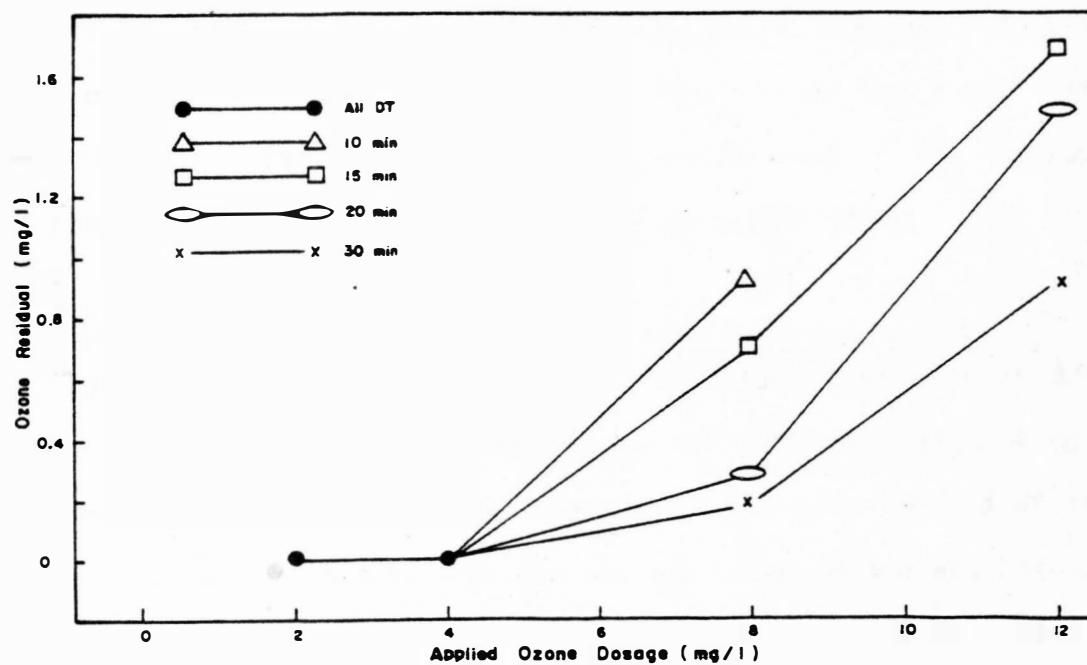


Figure 7. Ozone Residual Versus Ozone Dosage

residual existed. An analysis of variance of the ozone residual data, shown in Table C4, revealed the presence of a highly significant time-dosage interaction effect. This meant that it was necessary to observe the effects of ozone dosage at fixed levels of detention time and the effects of detention time at fixed levels of ozone dosage (18).

Detention Time Effects

An analysis of variance of the data, shown in Table C2, confirmed that the transfer efficiencies were not significantly affected by changes in detention time. This is in agreement with the findings of DeBoer (4).

Figure 7 indicates that high ozone residuals resulted from combinations of short detention times and high ozone dosages. This is also in conformance with DeBoer's (4) results. Ozone has a half life of 30 minutes or less in water and as a result, much of the residual ozone reverts back to oxygen at the longer detention times.

Ozone Demand

By observing transfer efficiencies and ozone residuals at dosages greater than 4 mg/l (the demand was not satisfied at a 4 mg/l dosage or less), it was possible to estimate the ozone demand of the raw water. It was estimated that the average ozone demand was between 5 and 6 mg/l. Since the primary ozone demand was exerted by iron and manganese, and since there is considerable variation in the raw water

iron concentration, there will be variation in the ozone demand of the raw water.

Temperature and pH

Temperature

The raw water, CC-2 effluent, and filter effluent temperatures were measured at each operating run. Since the average groundwater temperature was about 14°C (Appendix D) and the temperature within the treatment plant was about 20°C, it would be anticipated that the water temperature would increase as it flowed through the pilot plant. This is exactly what was observed during this investigation. It was observed that at the 5-minute detention time, the total increase through the pilot plant was 0.6°C, while at the 30-minute detention time, the total increase was 0.9°C.

pH

The pH of the raw water, CC-2 effluent, and filter effluent were all determined for each run. In order to analyze pH values, they were converted to an arithmetic scale since they are logarithmic expressions. The pH of a water, as indicated by equation 6, is defined as the negative logarithm of the hydrogen-ion concentrations.

$$\text{pH} = -\log_{10}(\text{H}^+) \quad (6)$$

$$\text{H}^+ = 10^{\exp(-\text{pH})} \quad (7)$$

The average pH of the groundwater was 6.75 (Appendix D) during this investigation. The corresponding hydrogen-ion concentrations for the

measured pH values are tabulated in Tables E1 and E3. These hydrogen-ion concentrations were then used as the basis for the statistical analyses.

In Figures 8 and 9, the mean pH values for the CC-2 and filter effluents, respectively, are shown as functions of applied ozone dosage. From Figure 8, it can be observed that at zero ozone dosage (aeration only), pH increased with increases in detention time. This can be attributed to the fact that when groundwater is aerated, carbon dioxide is stripped from the water causing the pH to rise. Also, as detention time increased, apparently more carbon dioxide is released causing further increases in pH.

In contact column two, the pH dropped sharply as the ozone dosage was increased from 0 to 4 mg/l but declined only slightly or remained almost constant with further increases in ozone dosage. Analysis of variance of the data, shown in Table E2, confirmed that a significant difference (5 per cent level) existed between the mean hydrogen-ion concentrations at the various ozone dosages for the contact column two effluent. Also, as illustrated in Figure 9 and confirmed by analysis of variance in Table E4, the pH of the filter effluent was significantly affected by changes in ozone dosage. A general decrease is noted with increasing ozone dosage.

Stoebner (17) has provided a possible explanation for the drop in pH as a result of the increase in ozone dosage. He observed that ozone has a greater tendency to react with hydroxyl ions (OH^-) than

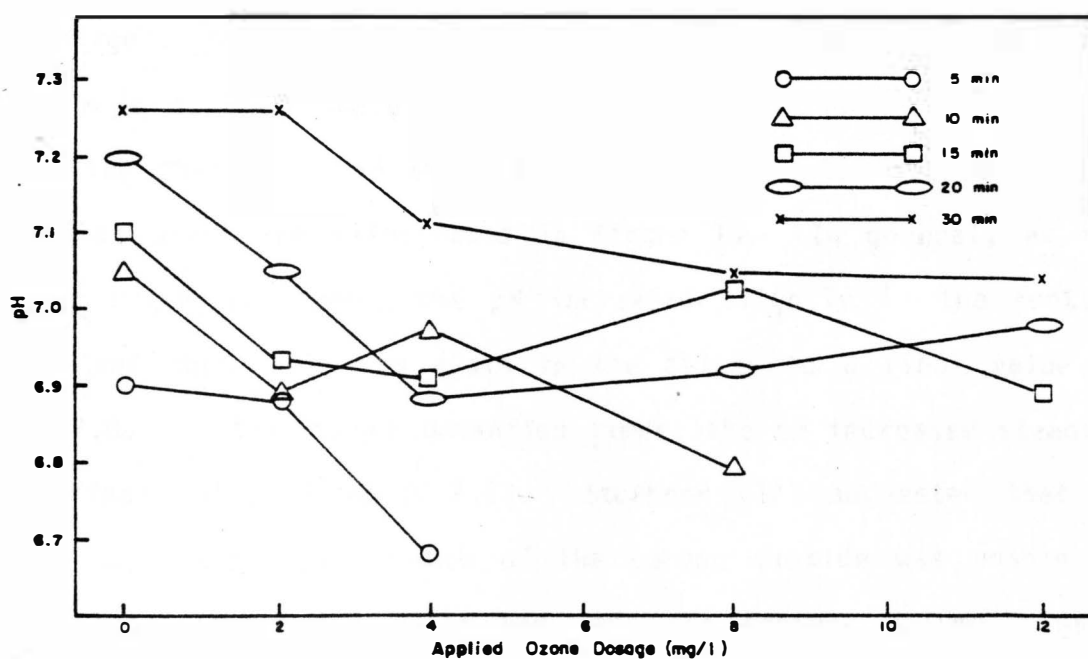


Figure 8. Contact Column Two Effluent pH Versus Ozone Dosage

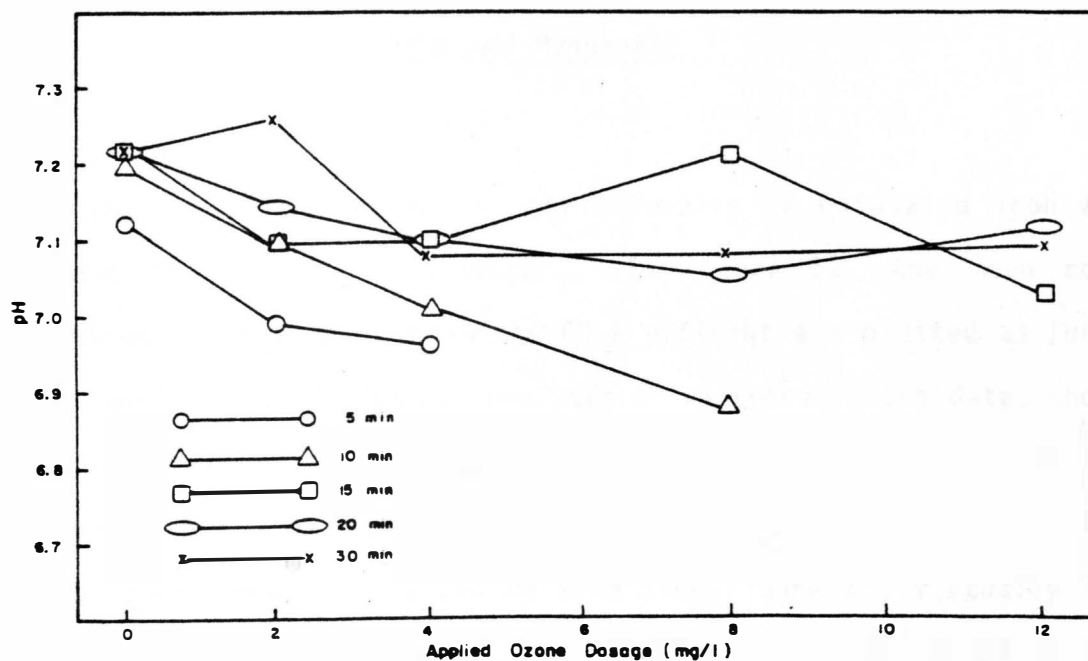


Figure 9. Filter Effluent pH Versus Ozone Dosage

does oxygen. Reducing the concentrations of hydroxyl ions in water will, in turn, lower the pH.

The changes in pH which occurred as the water flowed through the pilot plant are illustrated in Figure 10. In general, at the shorter detention times, the pH increased slightly in the contact column and then increased again in the filter to a final value of about 7.0. At the longer detention times, the pH increased steadily to a final value of about 7.13. Stoebner (17) suggested that at shorter detention times, much of the carbon dioxide was unable to escape until after the water had left the contact column. As a result, the reaction of ozone with the hydroxyl ions may have caused the increase in pH to be less pronounced in the contact column.

Iron and Manganese

Contact Columns Effluent

The ozonation system is very effective in oxidizing iron and manganese in the raw groundwater. In Figure 11, the mean concentrations of soluble iron in the CC-2 effluent are plotted as function of applied ozone dosage. Analysis of variance of the data, shown in Table F2, confirmed that a highly significant difference existed between soluble iron concentrations in the CC-2 effluent at the various ozone dosages. As can be seen from Figure 11, virtually all of the iron had been oxidized at the 2 mg/l ozone dosage except at the

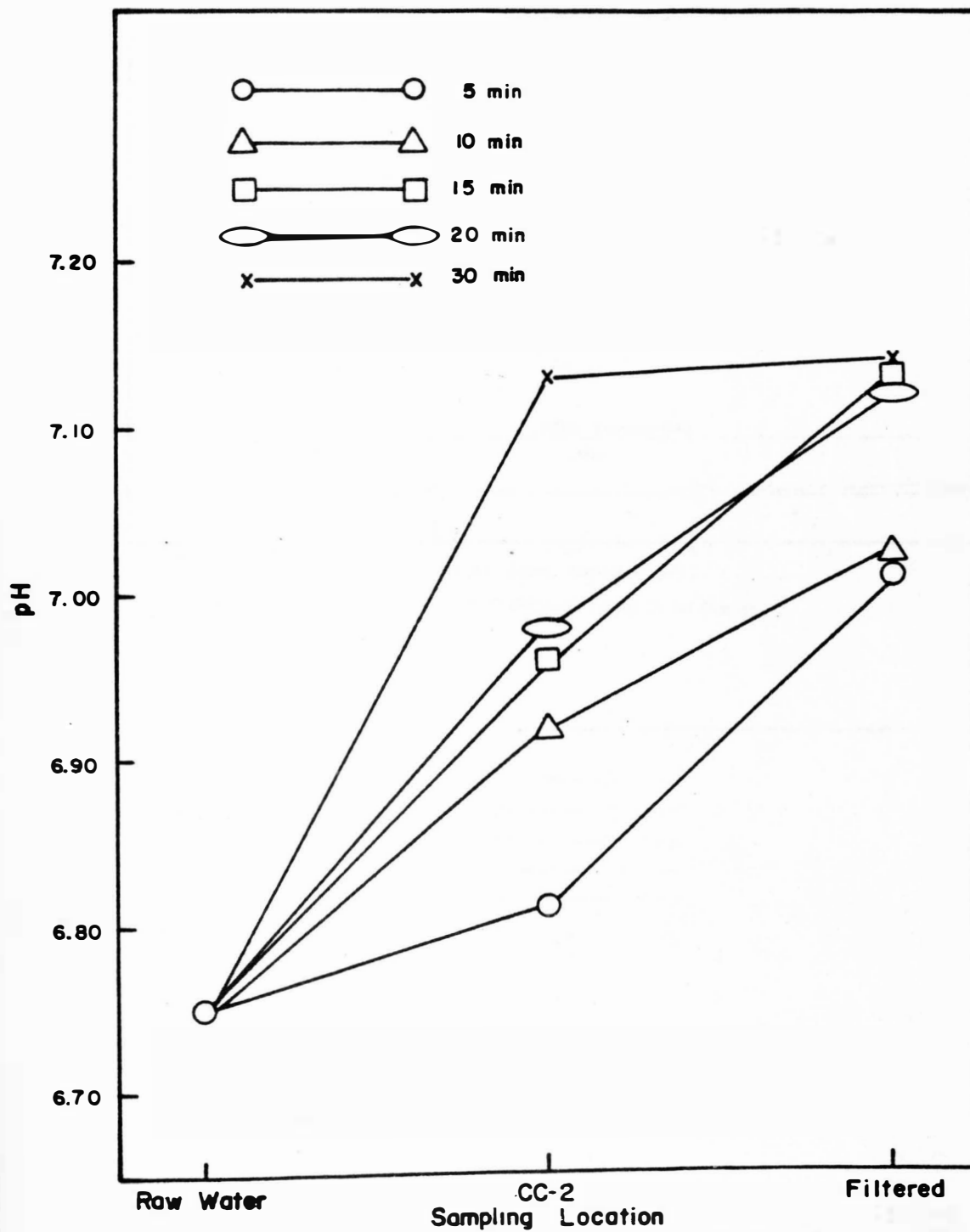


Figure 10. Water pH Versus Sampling Location

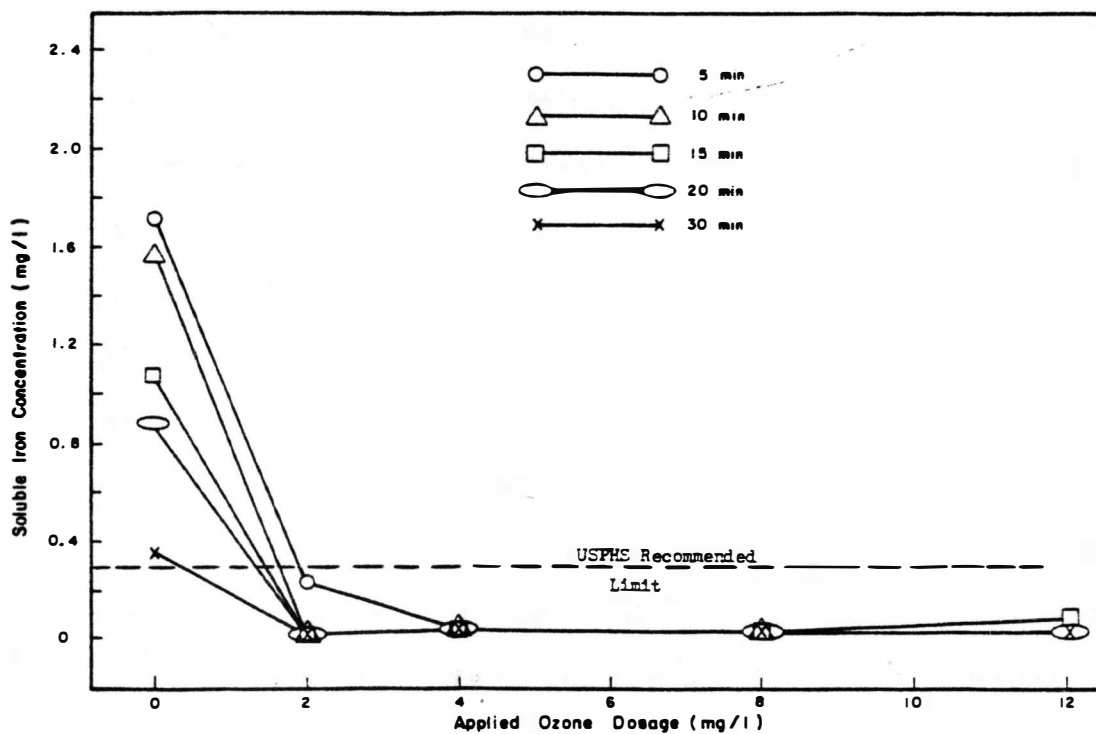


Figure 11. Soluble Iron in CC-2 Effluent Versus Ozone Dosage

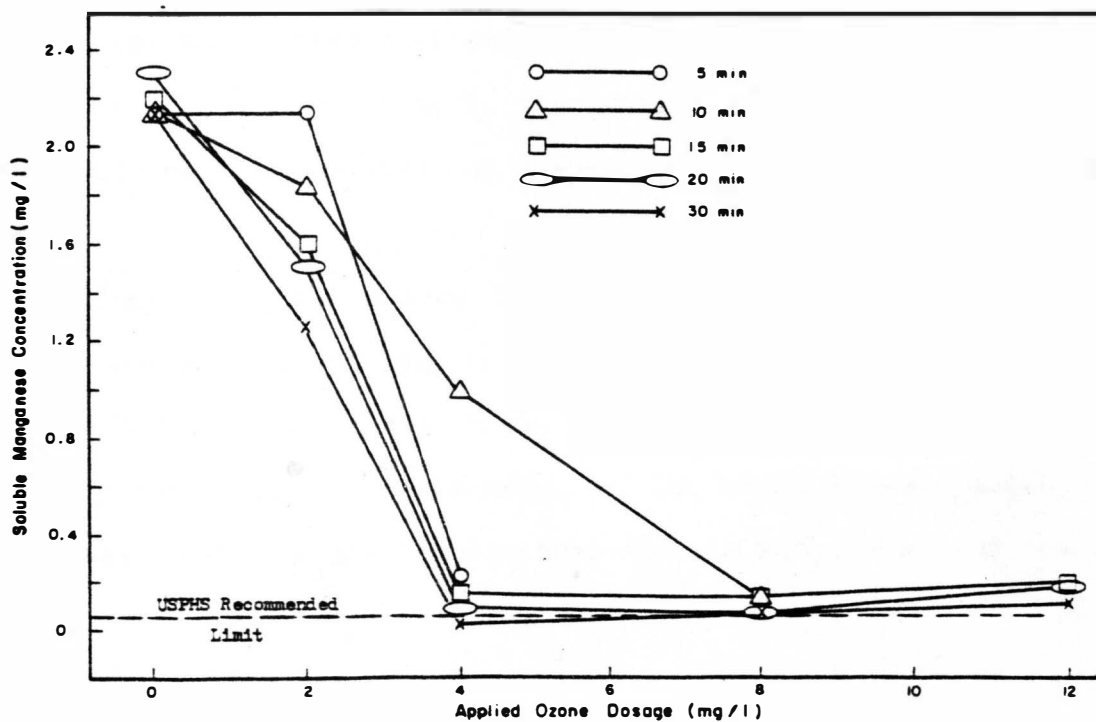


Figure 12. Soluble Manganese in CC-2 Effluent Versus Ozone Dosage

5-minute detention time. At the 4 mg/l dosage, virtually all of the iron (greater than 99 per cent) was oxidized at all detention times.

It is apparent that the concentrations of soluble iron in the CC-2 effluent decreased with increased detention time at the 0 mg/l dosage level (i.e. aeration only). This effect was much less pronounced at the 2 mg/l dosage level and did not exist at all beyond the 2 mg/l dosage level. An analysis of variance of the data revealed a highly significant effect of detention time on soluble iron concentration. Obviously, simple aeration was oxidizing most of the iron at the longer detention times. However, it was not possible to oxidize iron to the recommended limits with simple aeration.

In Figure 12, the mean concentrations of soluble manganese in the CC-2 effluent are plotted as functions of applied ozone dosage. From Figure 12 it can be observed that simple aeration or ozonation at the 2 mg/l level did not oxidize much of the manganese. However, raising the dosage to 4 mg/l greatly increased the oxidation of manganese. At a dosage of 8 mg/l, the soluble manganese was reduced to about 0.10 mg/l. This represents manganese oxidation of about 95 per cent.

Increasing the dosage beyond 8 mg/l actually increased the soluble manganese slightly. At the time samples were being collected, it was noted that at the higher ozone dosages the samples at a slightly purple color. Apparently, at the higher ozone dosages, the ozone was oxidizing the soluble manganese to MnO_2 first and then to

permanganate (MnO_4) which is soluble. This would explain the purple color of the samples. As a result, when the analysis was run on soluble manganese at the higher ozone dosages, the manganese in MnO_4 was being measured instead of the initial soluble manganese. This would indicate a "break-point" at which all the manganese is in an insoluble state and beyond which begins conversion to a soluble state again.

From Figure 12, it appears that detention time has a slight effect upon the oxidation of soluble manganese at the lower dosages but very little effect at higher dosages. The analysis of variance of the data, shown in Table F4, supports this conclusion.

In general, all of the soluble iron was effectively oxidized at the 4 mg/l dosage level while manganese was not effectively reduced until the dosage was increased beyond 4 mg/l. Furthermore, it is a well established fact that manganese is more difficult to oxidize than iron and this is certainly illustrated clearly by the higher ozone dosages required for manganese oxidation.

As pointed out earlier, the ozone demand of the raw groundwater is between 5 and 6 mg/l depending upon the raw water quality. The primary ozone demand is exerted by iron and manganese, therefore, the most probable optimum ozone dosage for iron and manganese removal is between 5 and 6 mg/l. Finally, the degree of iron and manganese oxidation was not greatly affected by the length of detention time in the optimum dosage range. These conclusions agree very well with the

observations made by Stoebner (17) during his investigation of using ozone to remove iron and manganese from the groundwater supply at Brookings, South Dakota.

Filter Effluent

The soluble iron concentrations in the filter effluent are presented in Table F5. From these data, it can be seen that regardless of ozone dosage or detention time, the mean soluble iron concentrations were never greater than 0.04 mg/l. This indicates that, even with simple aeration, nearly 99 per cent of the iron had been oxidized by the time it reached the filter. An analysis of variance of the data, shown in Table F6, confirmed that the mean concentrations of soluble iron were not significantly affected by changes in ozone dosage or detention time.

The total iron concentrations in the filter effluent are tabulated in Table F7. The mean total iron concentrations in the filter effluent varied between 0.02 and 0.11 mg/l, a range of values well below the USPHS drinking water standards. Concentrations of total iron in the filter effluent were only slightly lower during the ozonized runs than during simple aeration.

The concentrations of soluble and total manganese in the filter effluent are presented in Tables F9 and F11, respectively. Unfortunately, the data collected on soluble and total manganese concentrations were generally quite high and very erratic during the various runs. For total manganese, the mean concentrations in the

filter effluent were above the USPHS drinking water standards for nearly all dosages and detention times. Furthermore, an analysis of variance of the data, shown in Tables F10 and F12, confirmed that ozone dosage and detention time had no significant effect upon the concentration of soluble and total manganese in the filter effluent.

In most instances, at the 4 mg/l dosage and lower, the concentration of soluble manganese in the filter effluent was considerably lower than in the contact columns effluent. Obviously, additional oxidation of the manganese occurred as the water entered and passed through the filter. At the 8 mg/l dosage and higher, the soluble manganese concentrations in contact columns and filter effluent were roughly equal.

From Tables F9 and F11 it is noted that virtually all of the manganese was in the soluble state as it left the filter. This shows that the filter media was performing satisfactorily by removing virtually all the insoluble manganese. At the 4 mg/l dosage and below, complete oxidation was not taking place and some of the soluble manganese was passing through the filter. As noted previously, at the 8 mg/l dosage and above, there is strong indication that soluble permanganate was being formed which would, in turn, pass right through the filter. This all suggests that the 4 mg/l dosage was too low and an 8 mg/l dosage may have been slightly too high. The proper dosage is probably in the range of 5 to 6 mg/l.

Filter Performance

To study filter performance, the pilot plant was operated at an ozone dosage of 8 mg/l and since detention time was determined to have little effect upon oxidation, a 5-minute detention time was selected. A filter rate of 5 m/hr (2 gpm/ft²) was used. Table F13 includes the iron and manganese concentrations in the filter influent at various times during the run. The data reveal that the concentrations of total and soluble iron and manganese in the filter influent were fairly constant throughout the filter run.

In Figures 13 and 14, the iron and manganese concentrations in the filter effluent are plotted as functions of time. It is observed that, after approximately 24 hours, filter breakthrough was clearly evident. At 32 hours, total breakthrough had occurred. It is obvious from the figures that the breakthrough can be attributed to insoluble iron and manganese because soluble concentrations remained constant at 0.02 mg/l or less.

During the first 24 hours of the filter run, concentrations of iron and manganese in the filter effluent were less than the USPHS drinking water standards. However, at 28 hours, breakthrough occurred and the concentration of manganese in the filter effluent was three times greater than the USPHS limits. Based on these plots, the anthracite filter medium used would apparently result in filter runs of 24 hours or less.

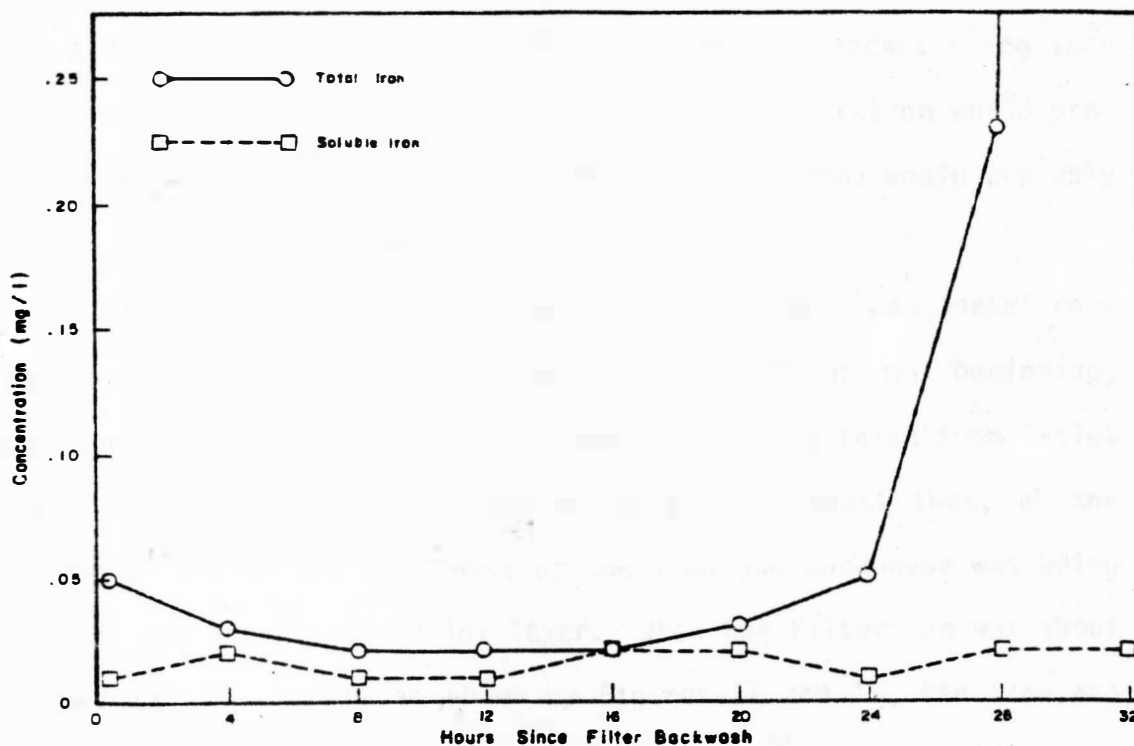


Figure 13. Iron Concentrations in the Filter Effluent Versus Time Since Backwash

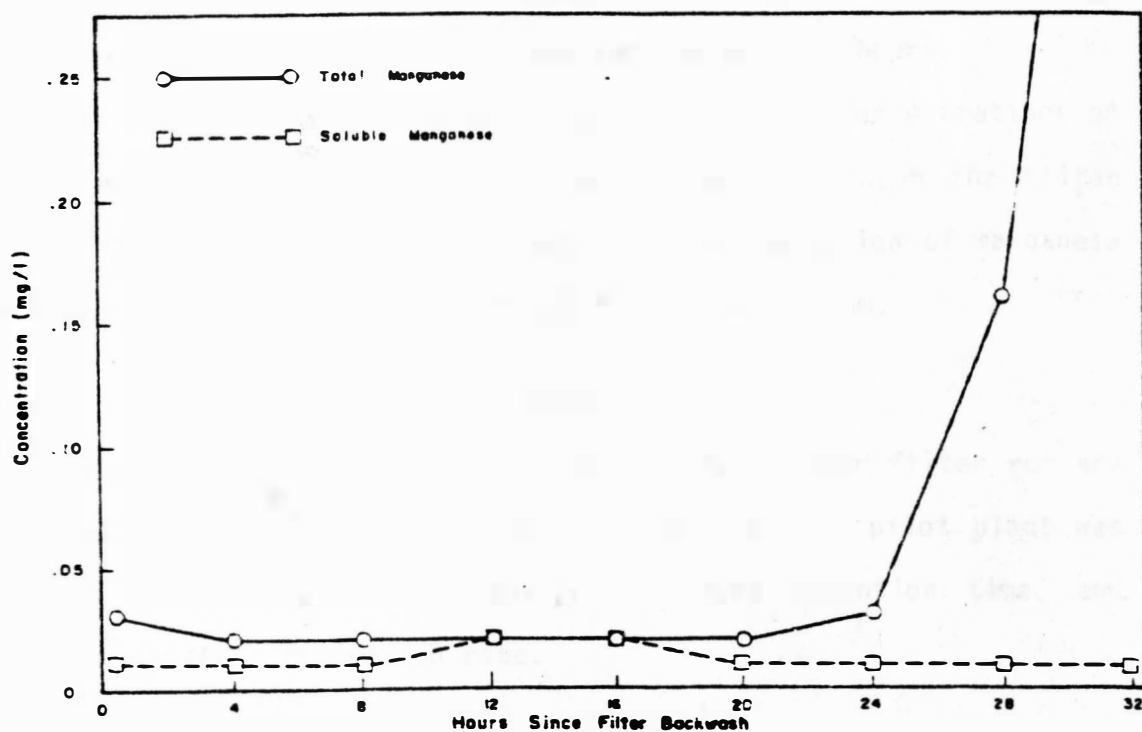


Figure 14. Manganese Concentrations in the Filter Effluent Versus Time Since Backwash

A full-scale ozonation/filtration treatment process using some type of coagulation and sedimentation prior to filtration would produce less of a load on the filter. This type of scheme would probably result in longer filter runs.

Figures 15 through 20 show the iron and manganese concentrations as functions of filter medium depth at the beginning, middle, and end of the filter run. These data were taken from Tables F15 and F16 in Appendix F. Figures 15 and 16 reveal that, at the beginning of the filter run, most of the iron and manganese was being removed by the top 7.6-cm (3-in) layer. When the filter run was about half over (at 16 hours), as shown by Figures 17 and 18, the iron and manganese removal profile had changed dramatically. At this point, most of the removal was occurring in the middle layers of the filter medium. Finally, as shown in Figures 19 and 20, the entire filter medium became saturated with iron and manganese at 32 hours.

As evidenced from Figures 16, 18, and 20, the concentrations of soluble manganese decreased as the water passed through the filter medium. This should seem to indicate that the oxidation of manganese continued as the water passed through the filter medium.

Filter Head Loss

The head loss data collected during the 32-hour filter run are presented in Table G1. During this filter run, the pilot plant was operated at an 8-mg/l ozone dosage, 5-minute detention time, and 5-m/hr (2 gpm/ft²) filtration rate.

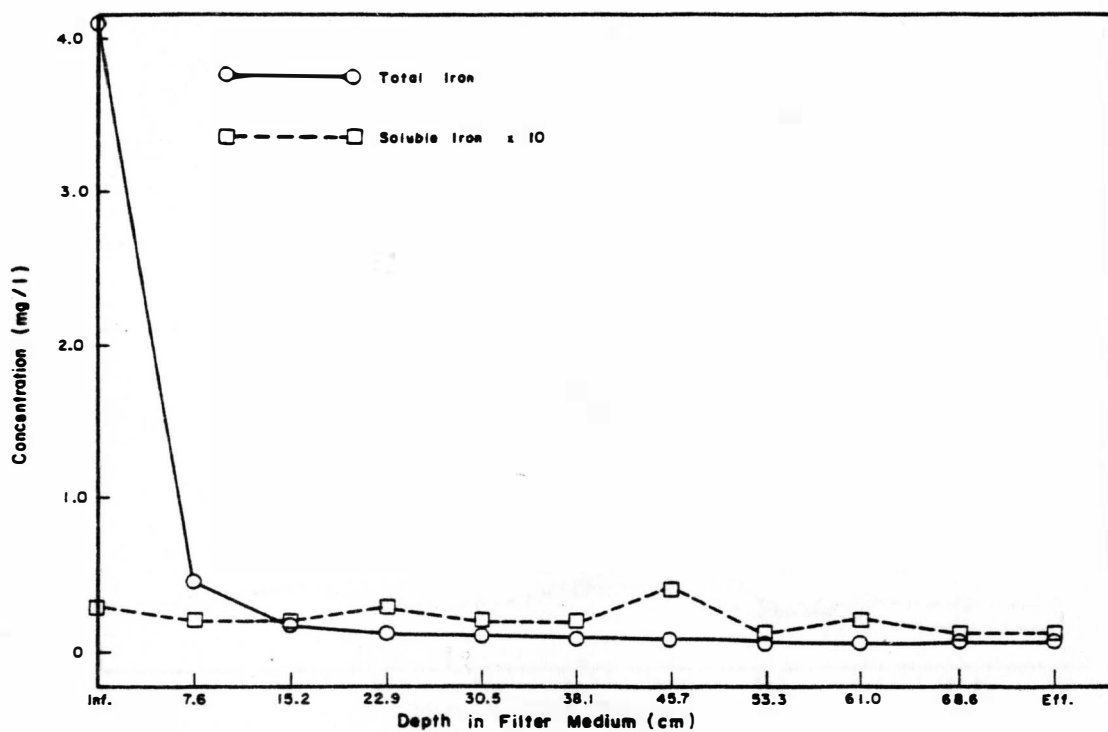


Figure 15. Iron Removal Profile Through Filter Medium (15 Minutes after Backwash)

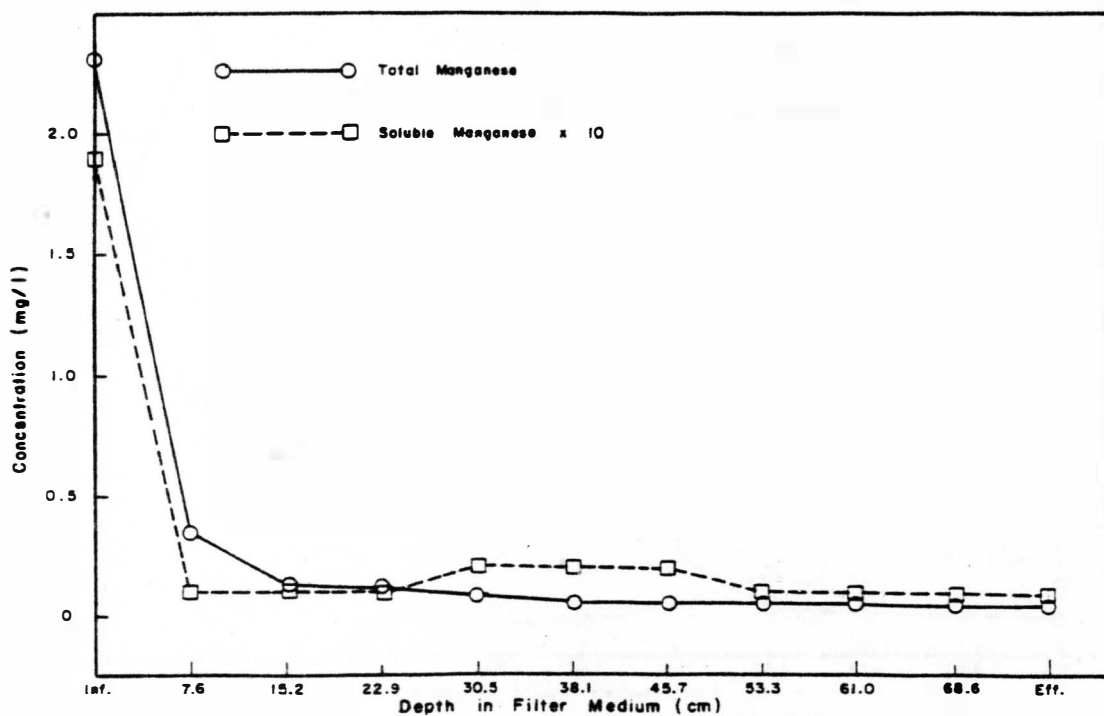


Figure 16. Manganese Removal Profile Through Filter Medium (15 Minutes after Backwash)

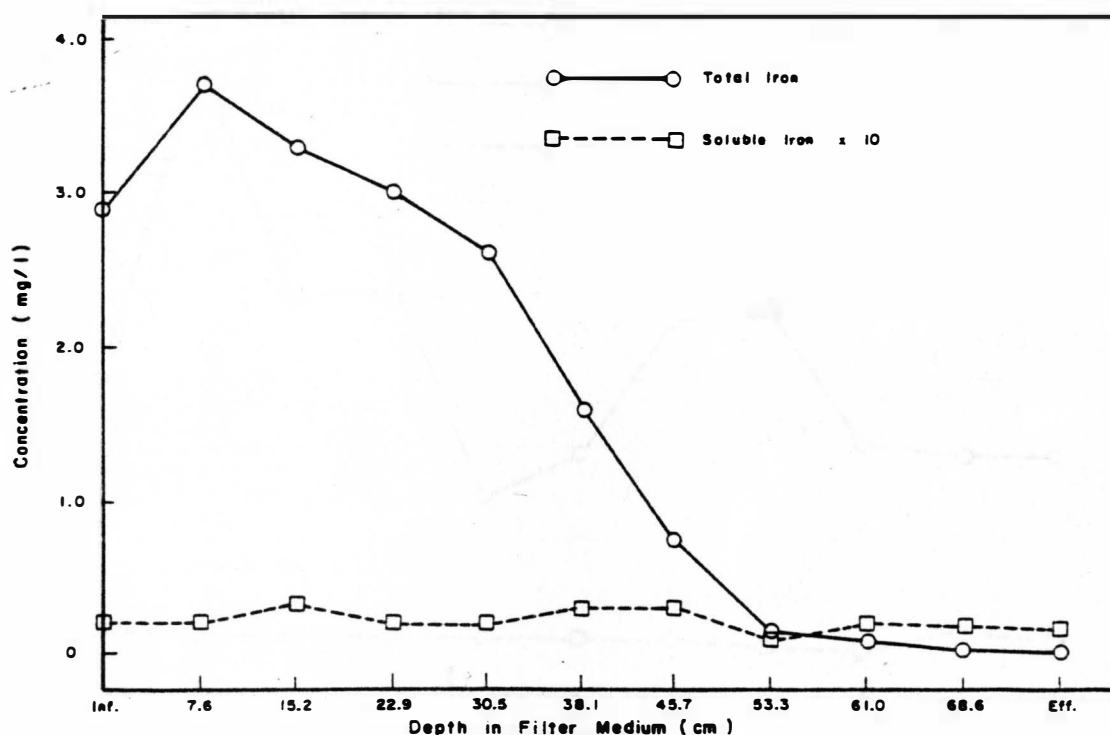


Figure 17. Iron Removal Profile Through Filter Medium (16 Hours after Backwash)

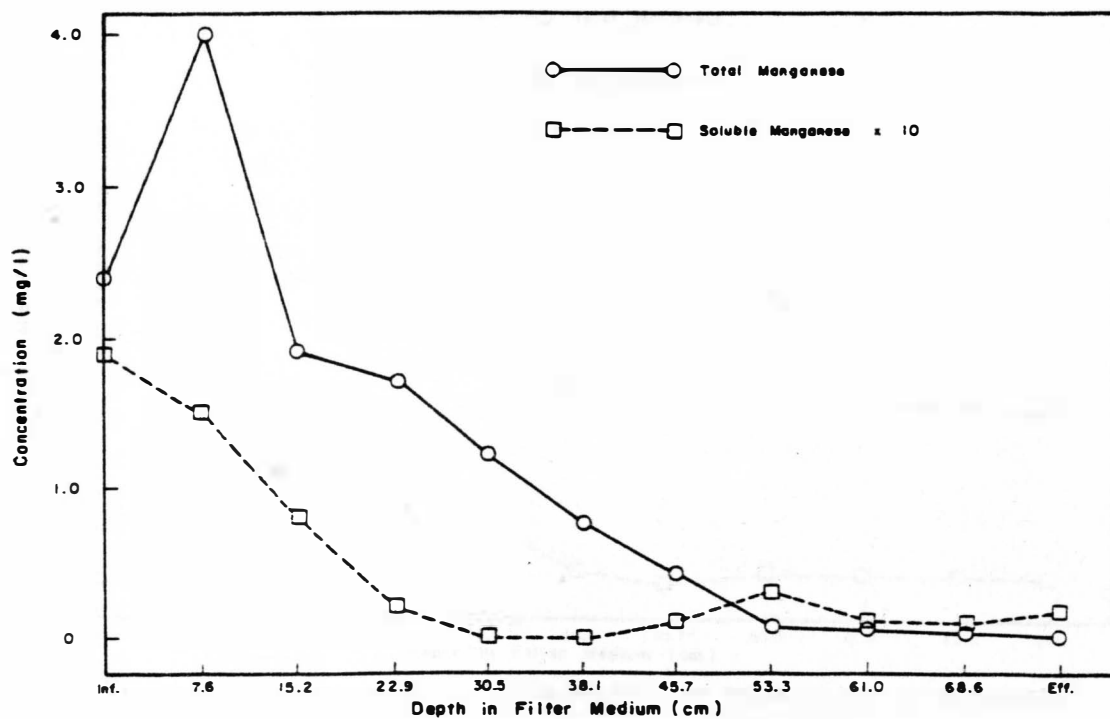


Figure 18. Manganese Removal Profile Through Filter Medium (16 Hours after Backwash)

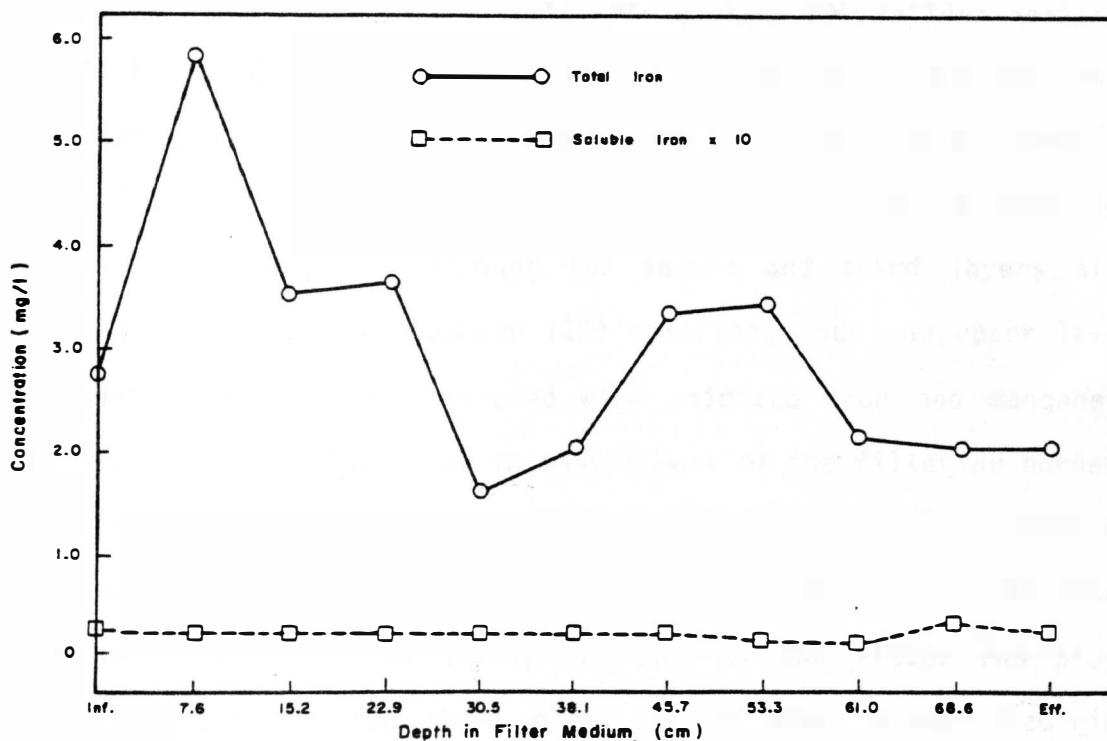


Figure 19. Iron Removal Profile Through Filter Medium (32 Hours after Backwash)

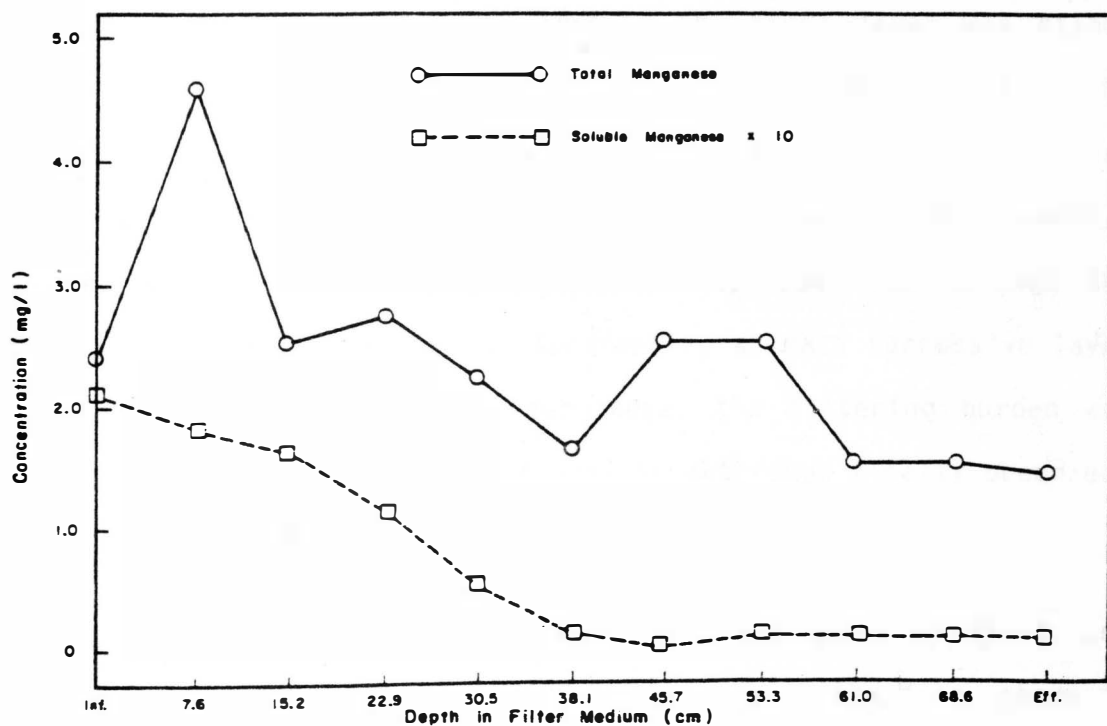


Figure 20. Manganese Removal Profile Through Filter Medium (32 Hours after Backwash)

Head losses through the filter are plotted for various sampling times in Figure 21. This figure shows that head losses are nonlinear with respect to depth and the largest amount of head loss occurs in the top layer of the filter. However, as the filter run progressed, the amount of head loss through the second and third layers also became quite large. As Stoebner (17) observed, once the upper layer of filter medium became saturated with oxidized iron and manganese particles, the lower layer had to assume more of the filtering burden.

Figure 22 shows a plot of total filter head loss versus time or volume of water filtered. In general, the rate of increase in total filter head loss remained fairly constant as the filter run progressed. Figure 22 also shows plots of the head losses occurring through each of the first three media layers as functions of time. The rate of head loss increase through the first layer was steady for the first 16 hours then tapered off. After 16 hours into the filter run, the top layer became completely saturated and the head loss in the second layer of filter medium began to increase rapidly. When the second layer approached saturation, head loss through the third layer began to rise also. Apparently, as each successive layer became saturated with iron and manganese, the filtering burden was passed on to the next lower layer until breakthrough finally occurred.

Chlorine Demand

The chlorine demand data collected during the 66 operating runs are tabulated in Table H1. Analysis of variance of the data, shown in

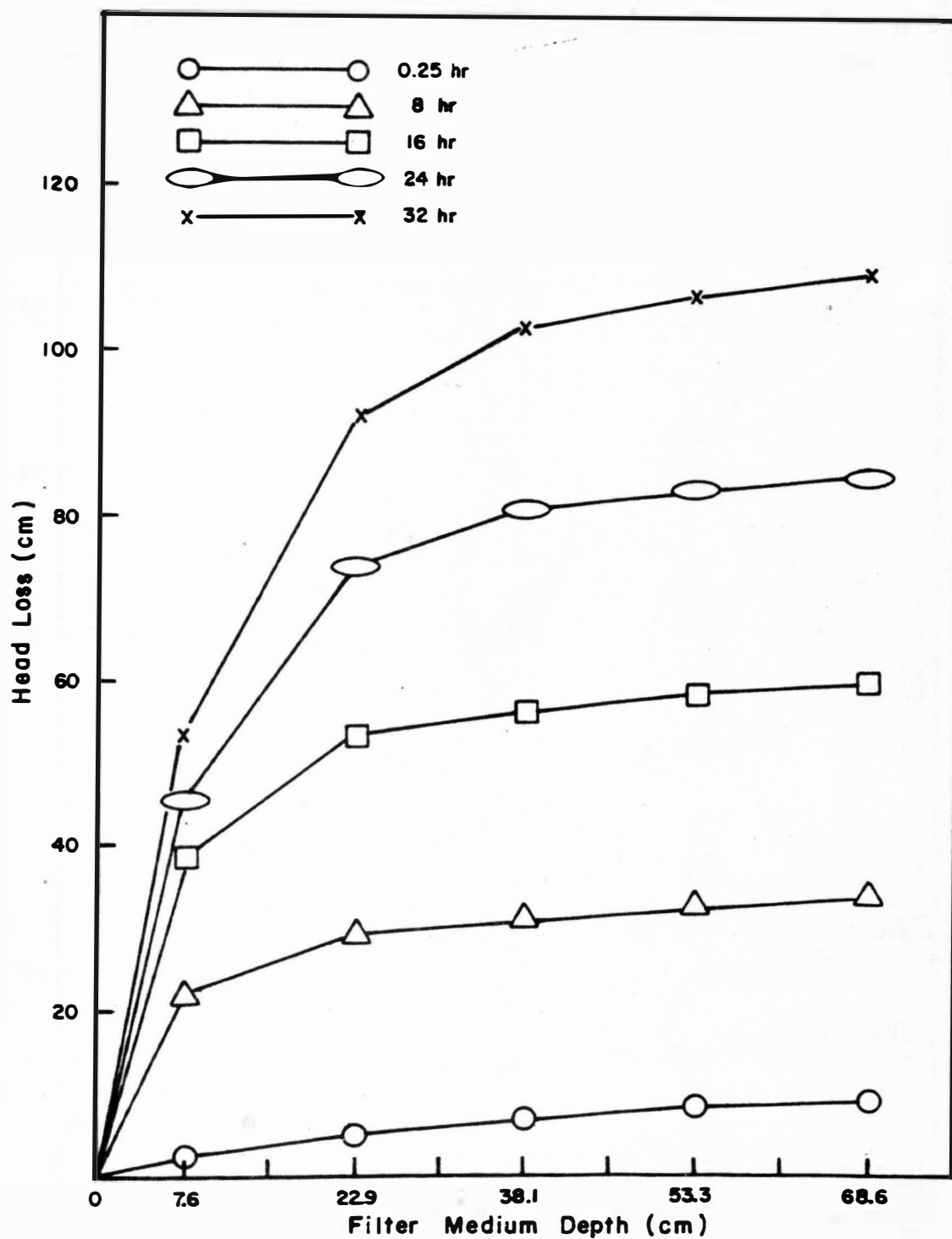


Figure 21. Head Loss Through Filter Medium

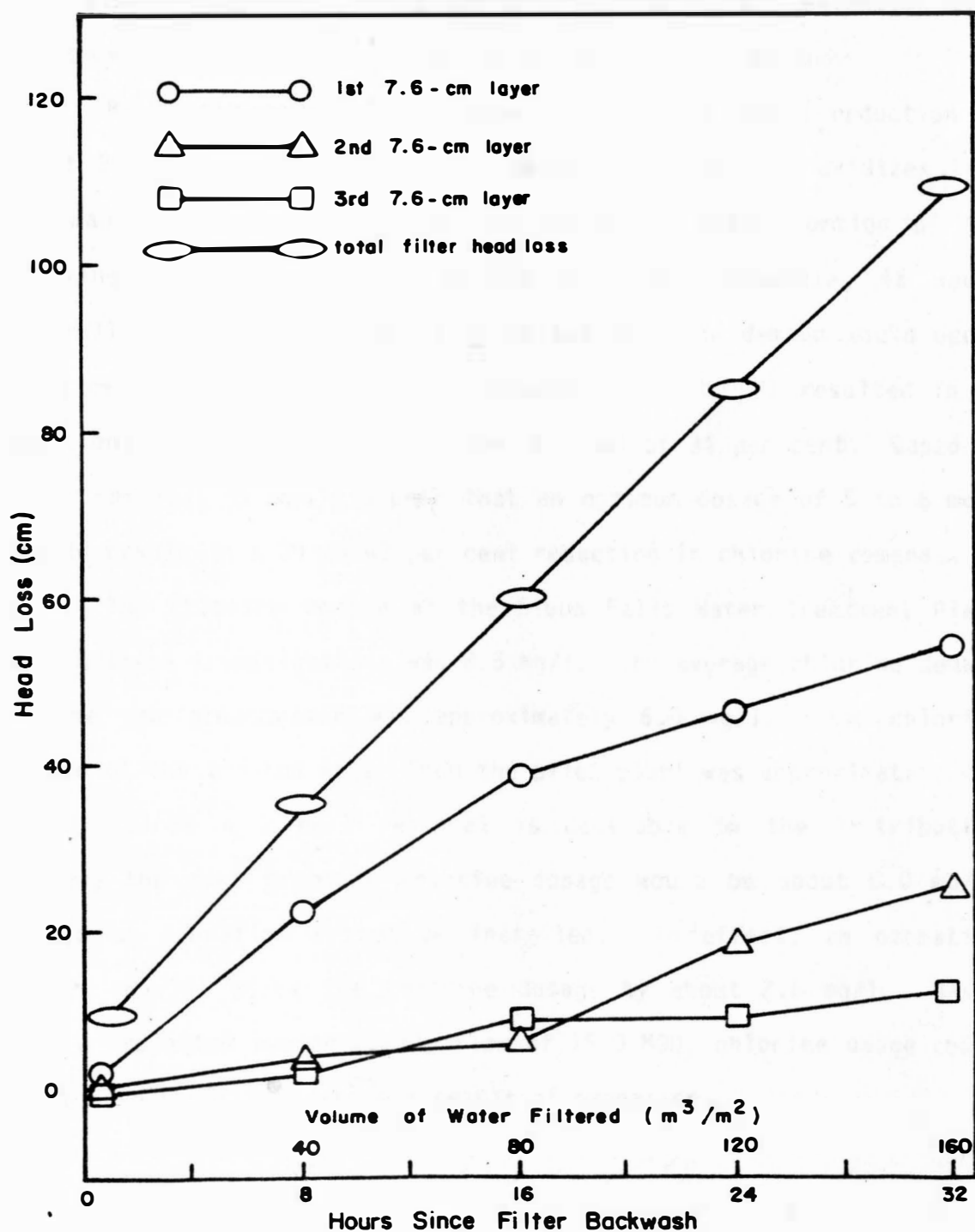


Figure 22. Filter Head Loss Versus Volume of Water Filtered

Table H2, revealed that significant differences existed between the mean chlorine demands at the various ozone dosages. Detention time was shown to have no significant effect on chlorine demand.

By simply aerating the water, a chlorine demand reduction of about 26 per cent was achieved. Aeration, in itself, oxidizes iron and manganese from groundwater and because a major portion of the chlorine demand is exerted by the iron and manganese, it would naturally follow that a reduction in the chlorine demand would occur as a result of aeration. Ozone dosages up to 8 mg/l resulted in an additional 8 per cent reduction for a total of 34 per cent. Based on these results, it would appear that an optimum dosage of 5 to 6 mg/l should result in a 30 to 40 per cent reduction in chlorine demand.

The chlorine dosage at the Sioux Falls Water Treatment Plant during these investigations was 8.5 mg/l. The average chlorine demand of the raw groundwater was approximately 6.0 mg/l. The chlorine demand of the treated water from the pilot plant was approximately 4.0 mg/l. Since a 2 mg/l residual is desirable in the distribution system, the most probable chlorine dosage would be about 6.0 mg/l, should an ozonation system be installed. In effect, an ozonation system should reduce the chlorine dosage by about 2.5 mg/l. Based upon a projected average daily flow of 15.0 MGD, chlorine usage could be reduced by 57 tons/yr as a result of ozonation.

Cost of Ozonation

The total cost of an ozonation system can be separated into a construction cost and an operating cost. The construction cost consists of the ozone generation system and the ozone contact chamber. Operating costs consist of expenditures for energy, labor, maintenance, and materials.

Based on the studies described herein, an ozone generation system capable of providing 8 mg/l ozone at design flow would be required along with a contact chamber sized on the basis of providing a 5-minute detention time. Using the design capacity of the Sioux Falls Water Treatment Plant of 196820 m³/day (52 MGD), an ozone generation capacity of 1574 kg/day (3470 lb/day) and a contact chamber volume of 683 m³ (24234 ft³) would be required. The details of the cost analysis calculations can be found in Appendix J.

In estimating the cost of installing and operating an ozonation system, cost curves developed by the United States Environmental Protection Agency (EPA) were used (7). At generation rates greater than 45.4 kg/day (100 lb/day), pure oxygen generated on-site is the feed for the ozone generator. The manufactured equipment cost for ozone generation includes the gas preparation equipment, oxygen generation equipment, the ozone generator, dissolution equipment, off gas recycling equipment, electrical and instrumentation costs, and all required safety and monitoring equipment. All ozone-generating equipment was considered to be housed, but oxygen-generating equipment would be outside on a concrete slab.

The ozone contact chamber would consist of a covered, reinforced concrete structure with a liquid depth of 18 ft, and a length-to-width ratio of approximately 2:1. Partitions would be utilized within the chamber to assure uniform flow distribution.

In the EPA cost estimate, it was assumed that ozone generation using oxygen feed would require 16.5 kW-hr/kg (7.5 kW-hr/lb) of ozone produced. These figures include oxygen generation, ozone generation, and ozone dissolution. To determine the annual energy cost, a unit price of \$0.035/kW-hr was assumed. Labor requirements for periodic maintenance of the ozone generating equipment and contact chamber were converted to annual cost using a labor rate of \$10/hr. Maintenance material requirements are for periodic equipment repair and replacement of parts. Based upon manufacturers' recommendations, an annual maintenance material requirement of 1 per cent of construction cost was utilized.

Since the EPA cost curves were based on October 1978 values, it was necessary to update the costs using indices published by Engineering News Record (5) and by the United States Department of Labor (11). With these indices it was possible to update the costs to April 1981 prices. The calculations involved in the estimating and updating processes are presented in Appendix J, and the results are summarized in Table 2. From this summary it can be seen that the total cost of constructing the ozonation system was estimated to be

Table 2. Cost of Constructing and Operating an Ozonation System

Construction Costs	for Ozone Generation System	Manufactured Equipment	\$ 2,068,450
		Concrete	\$ 3,120
		Steel	\$ 3,070
		Labor	\$ 337,720
		Housing	\$ 53,720
		Miscellaneous and Contingency	\$ 369,910
	for Ozone Contact Chamber	Excavation and Sitework	\$ 3,190
		Concrete	\$ 11,460
		Steel	\$ 18,870
		Labor	\$ 24,200
		Miscellaneous and Contingency	\$ 8,660
	Total Construction Cost		\$ 2,902,370
Operation and Maintenance Costs	Maintenance Materials		\$ 41,740/yr
	Electrical Energy		\$ 96,890/yr
	Labor		\$ 29,200/yr
	Total Operation and Maintenance Cost		\$ 167,830/yr

Note: All calculations were based upon a maximum design flow of 52 MGD except for electrical energy costs. Electrical energy costs were based upon projected average flows.

Table 3. Total Annual Cost of Ozonation at Various Interest Rates

Interest Rate per cent	Capital Recovery Factor	Annual Repayment on Construction Cost \$/yr	Total Annual Cost \$/yr	O and M Cost per 3.79 m ³ (1000 gal) ¢	Total Annual Cost per (1000 gal) ¢
7	0.09439	273,950	441,780	3.1	8.1
8	0.10185	295,610	463,440	3.1	8.5
9	0.10955	317,950	485,780	3.1	8.9
10	0.11746	340,910	508,740	3.1	9.3
11	0.12558	364,480	532,310	3.1	9.7
12	0.13388	388,570	556,400	3.1	10.2
13	0.14235	413,150	580,980	3.1	10.6
14	0.15099	438,230	606,060	3.1	11.1
15	0.15976	463,680	631,510	3.1	11.5
16	0.16867	489,540	657,370	3.1	12.0
17	0.17769	515,720	683,550	3.1	12.5
18	0.18682	542,220	710,050	3.1	13.0

Note: total construction cost = \$2,902,370

annual operation and maintenance cost = \$167,830

Costs per gallons treated are based upon a projected average flow of 15 MGD.

CONCLUSIONS

Based upon the results of this investigation, the following conclusions were made:

1. The transfer efficiency of the ozone contacting system decreased significantly with increases in ozone dosage, but detention time had no significant effect on transfer efficiency.
2. The temperature of the water was not affected by ozone dosage but did increase with increased detention times. The pH tended to decrease slightly with increased dosage at any given detention time. The pH generally increased as the water flowed through the pilot plant as a result of carbon dioxide liberation, primarily due to aeration.
3. The degree of iron and manganese oxidation was greatly affected by changes in ozone dosage but was not greatly affected by changes in detention time. A 5-minute detention time appears to be sufficient.
4. Iron was totally oxidized at an ozone dosage of 4 mg/l while manganese was not effectively oxidized until the dosage was increased beyond 4 mg/l. At dosages of 8 mg/l and beyond, formation of soluble permanganate began. This would indicate that the optimum dosage is slightly less than 8 mg/l and based upon ozone demand is probably in the range of 5 to 6 mg/l.

5. Based upon a present average daly flow of 12.25 MGD, the optimum dosage (5 to 6 mg/l) is equivalent to 511 to 613 lbs O₃/day. A full-scale ozonation system should have the capacity to provide 8 mg/l at design flow (52 MGD). A unit capable of providing 3500 lbs/day would be specified.
6. The anthracite filter medium was effective in removing the insoluble iron and manganese.
7. At a filtering rate of 5 m/hr (2 gpm/ft²), the maximum practical length of filter run would be about 20 hours.
8. Head loss through the pilot filter was nonlinear with respect to media depth with the largest amount of head loss occurring in the upper layers of the filter medium.
9. The rate of increase in total filter head loss remained constant with increases in filtration time after backwash.
10. Ozonation of the groundwater resulted in a 34 per cent reduction in the chlorine demand of the water (6.0 to 4.0 mg/l). On a full scale, an ozonation system would preclude the need for 57 tons/yr of chlorine based upon projected average flows.
11. Based upon April 1981 prices, the operation and maintenance cost of an ozonation system for the city of Sioux Falls was estimated to be 3.1¢ per 3.79 m³ (1000 gal). At an interest rate of 12 per cent, the total annual cost was estimated to be 10.2¢ per 1000 gallons.

RECOMMENDATIONS FOR FUTURE STUDIES

The following recommendations are made for future studies involving the ozone pilot plant.

1. The results of this study indicated that ozonation was effective in reducing the chlorine demand of groundwater. It would be interesting to study the effect of ozonation on chlorine demand of a surface water supply.
2. Since the cost of energy is a major factor in an ozonation system, it would be interesting to study the energy efficiency of the pilot plant. This could be accomplished by incorporating a watt meter into the system.

LITERATURE CITED

1. Al-Layla, M.; Ahmad, S.; and Middlebrooks, E. J., Water Supply Engineering Design, Ann Arbor Science, Inc., Ann Arbor, Michigan, 1977, pp. 138, 255.
2. Babbitt, H. E.; and Doland, J. J., Water Supply Engineering, 5th Ed., McGraw-Hill Book Co., Inc., New York, 1955.
3. Bean, E. L., "Quality Goals for Potable Water", American Water Works Association Journal, 60, 12, pp. 1317-1322, 1968.
4. DeBoer, D. E., Design, Construction and Performance Evaluation of an Ozonation Pilot Plant, Master of Science Thesis, South Dakota State University, Brookings, South Dakota, 1980.
5. "ENR Market Trends", Engineering News Record, 217, 10, p. 58, 1981.
6. Furgason, R. R.; and Day, R. O., "Iron and Manganese Removal with Ozone", Water and Sewage Works, 122, 6, pp. 42-47, 1975; 7, pp. 61-63, 1975.
7. Gumerman, R. C.; Culp, R. L.; and Hansen, S. P., Estimating Water Treatment Costs, Volume 2, Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, Ohio, August 1979.
8. Hammer, M. J., Water and Waste-Water Technology, John Wiley and Sons, Inc., New York, 1975, p. 32.
9. Hann, V. A., "Ozone Treatment of Water", American Water Works Association Journal, 35, 5, pp. 585-591, 1943.
10. Kirk, J. T.; and Anthony, R. M.; "Manganese Removal Using Ozone", Presented at the Annual Meeting of the North Central Section, American Water Works Association, Unpublished, 1980.
11. News, Bureau of Labor Statistics, United States Department of Labor, Washington, D.C., April, 1981.
12. O'Connor, J. T., "Iron and Manganese", Water Quality and Treatment, 3rd Ed., McGraw-Hill Book Co., New York, 1971, pp. 378-396.
13. Public Health Service Drinking Water Standards, United States Department of Health, Education, and Welfare, Publication No. 956, Government Printing Office, Washington, D.C., 1962.

14. Quail, S. J., The Effectiveness of Aeration, Potassium Permanganate Oxidation, and Filtration on Removal of Iron and Manganese from Ground Water, Master of Science Thesis, South Dakota State University, Brookings, South Dakota, 1980.
15. Sawyer, C. N.; and McCarty, P. L., Chemistry for Environmental Engineers, 3rd Ed., McGraw-Hill Book Company, Inc., New York, 1978.
16. Standard Methods for the Examination of Water and Wastewater, 14th Ed., American Public Health Association, Inc., New York, 1975.
17. Stoebner, R. A., Ozonation of a Municipal Groundwater Supply to Reduce Iron, Manganese, and Trihalomethane Formation, Master of Science Thesis, South Dakota State University, Brookings, South Dakota, 1980.
18. Walpole, R. E.; and Myers, R. H., Probability and Statistics for Engineers and Scientists, 2nd Ed., Macmillian Publishing Company, Inc., New York, 1978.

APPENDIX A
LIST OF SYMBOLS AND ABBREVIATIONS

LIST OF SYMBOLS AND ABBREVIATIONS

AWWA = American Water Works Association

BLS = Bureau of Labor Statistics

C_i = ozone concentration in ozonized gas (mg O_3 /l gas)

CC-1 = contact column number one

CC-2 = contact column number two

D = applied ozone dosage (mg O_3 /l H_2O)

E = ozone transfer efficiency

ENR = Engineering News Record

Q_g = gas flow rate (slpm)

Q_l = liquid flow rate (lpm)

slpm = standard liters per minute

T = detention time (min)

USPHS = United States Public Health Service

V = liquid volume of contact columns (liters)

W_i = weight of ozone entering the contact columns via the contacting gas (g/hr)

W_o = weight of ozone leaving the contact columns via the off-gas (g/hr)

APPENDIX B
EXPERIMENTAL CALCULATIONS

EXPERIMENTAL CALCULATIONS

A. Ozone Concentration

$$C = \frac{\text{Wt } O_3}{V}$$

where: C = ozone concentration (mg O_3 /l gas)

Wt O_3 = weight of ozone trapped in the potassium iodide solution (mg)

V = volume of gas that passed through the wet-test meter corrected to standard temperature and pressure

$$\text{Wt } O_3 = (N)(\text{ml titrant})(24)$$

where: N = normality of sodium thiosulfate solution

$$V = (V_1)(P_1/P_2)(T_2/T_1)$$

where: V = volume of gas that passed through the wet-test meter corrected to standard temperature and pressure

V_1 = actual volume of gas that passed through the wet-test meter (liters)

P_1 = adjusted pressure = atmospheric pressure + wet-test meter manometer deflection - water vapor pressure = _____ cm H_2O

P_2 = standard pressure = 1 atmosphere = 1033 cm H_2O

T_1 = room temperature = _____ $^{\circ}C$ + 273 = _____ $^{\circ}K$

T_2 = standard temperature = $25^{\circ}C$ + 273 = $298^{\circ}K$

B. Gas Flow Rate

$$Q_g = (Q_1)(P_3/P_4) \sqrt{T_3/T_1} (T_2/T_3)$$

where: Q_g = gas flow rate corrected to standard temperature and pressure (slpm)

Q_1 = actual gas flow rate (lpm)

P_3 = gage backpressure + barometric pressure (mm Hg)

$$P_4 = \text{calibration gage pressure} + \text{standard pressure} = 776 \text{ mm Hg} + 760 \text{ mm Hg} = 1536 \text{ mm Hg}$$

$$T_1 = \text{room temperature} = \text{ } ^\circ\text{C} + 273 = \text{ } ^\circ\text{K}$$

$$T_2 = \text{standard temperature} = 25^\circ\text{C} + 273 = 298^\circ\text{K}$$

$$T_3 = \text{calibration temperature} = 21^\circ\text{C} + 273 = 294^\circ\text{K}$$

C. Ozone Mass Flow Rate

$$W = (Q_g)(C) \left(\frac{60 \text{ min}}{\text{hr}} \right) \left(\frac{\text{g}}{1000 \text{ mg}} \right) = (0.06)(Q_g)(C)$$

where: W = ozone mass flow rate (g/hr)

Q_g = gas flow rate (slpm)

C = ozone concentration (mg O_3 /l gas)

D. Transfer Efficiency

$$E = (100)(W_i - W_o)/W_i$$

$$W_i = (0.06)(Q_g)(C_i)$$

$$W_o = (0.06)(Q_g)(C_o)$$

where: E = ozone transfer efficiency (per cent)

W_i = mass flow rate of ozone entering the contact columns via the contacting gas (g/hr)

W_o = mass flow rate of ozone leaving the contact columns via the off-gas (g/hr)

Q_g = gas flow rate (slpm)

C_i = ozone concentration in the contacting gas (mg O_3 /l air)

C_o = ozone concentration in the off-gas (mg O_3 /l air)

E. Applied Ozone Dosage

$$D = (C_i)(Q_g/Q_1)$$

where: D = applied ozone dosage (mg/l)

C_i = ozone concentration in the contacting gas (mg O_3 /l air)

Q_g = ozonized air flow rate (slpm)

Q_1 = water flow rate (lpm)

F. Ozone Residual

$$OR = \frac{Wt\ O_3}{V_o}$$

$$Wt\ O_3 = (N)(ml\ titrant)(24)$$

where: OR = ozone residual (mg O_3 /l H_2O)

Wt O_3 = weight of ozone trapped in the potassium iodide solution (mg)

V_o = volume of water sample (liters)

N = normality of the sodium thiosulfate titrant

G. Chlorine Demand

$$Cl_d = Cl_a - Cl_r$$

where: Cl_d = chlorine demand (mg Cl/l H_2O)

Cl_a = applied chlorine dose = 8.5 mg Cl/l H_2O

Cl_r = chlorine residual (mg Cl/l H_2O)

APPENDIX C
TRANSFER EFFICIENCY AND OZONE RESIDUAL:
RESULTS AND STATISTICAL ANALYSES

Table C1. Transfer Efficiencies (per cent)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	2	95.9	94.5	93.9	91.9	90.6
		81.0	91.0	94.2	90.5	90.0
		90.7	84.8	89.0	90.2	91.0
		<u>89.2</u>	<u>90.1</u>	<u>92.4</u>	<u>90.9</u>	<u>90.5</u>
	4	90.3	90.1	90.9	91.2	89.7
		78.0	79.8	81.0	89.0	89.3
		86.3	85.1	84.2	86.6	84.3
		<u>84.9</u>	<u>85.0</u>	<u>85.4</u>	<u>88.9</u>	<u>87.9</u>
	8		79.0	84.7	91.9	87.5
			77.9	72.0	76.4	81.4
			81.3	76.5	78.8	82.9
			<u>79.4</u>	<u>77.7</u>	<u>82.4</u>	<u>83.9</u>
	12	1st rep 2nd rep 3rd rep mean		81.3	82.8	74.5
				67.6	70.0	70.7
				78.8	77.0	76.6
				<u>75.9</u>	<u>76.6</u>	<u>73.9</u>

Table C2. Analysis of Variance of Transfer Efficiency Data

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	1493.2208	3	497.7403	20.03
Time	60.6186	4	15.1547	0.61
Interaction	80.3742	9	8.9308	0.36
Error	844.7333	34	24.8510	
Total	2493.1804	50		

** significant at the 1 per cent level

Table C3. Ozone Residuals (mg O₃/l H₂O)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	2	0.00	0.00	0.00	0.30	0.00
		0.00	0.00	0.00	0.00	0.30
		0.00	0.00	0.00	0.00	0.00
		<u>0.00</u>	<u>0.00</u>	<u>0.00</u>	<u>0.00</u>	<u>0.00</u>
	4	0.00	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.30
		0.00	0.00	0.00	0.00	0.00
		<u>0.00</u>	<u>0.00</u>	<u>0.00</u>	<u>0.00</u>	<u>0.30</u>
	8		1.10	0.65	0.30	0.30
			1.00	0.90	0.41	0.10
			0.68	0.51	0.10	0.10
			<u>0.93</u>	<u>0.69</u>	<u>0.27</u>	<u>0.17</u>
	12	1st rep 2nd rep 3rd rep mean		1.48	1.19	0.90
				2.19	1.80	1.05
				1.40	1.40	0.82
				<u>1.69</u>	<u>1.46</u>	<u>0.92</u>

Table C4. Analysis of Variance of Ozone Residual Data

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F	
Dosage	12.3811	3	4.1270	165.48	**
Time	0.8495	4	0.2124	8.52	**
Interaction	1.2221	9	0.1356	5.44	**
Error	0.8479	34	0.2249		
Total	16.0666	50			

** significant at the 1 per cent level

APPENDIX D
RAW WATER SAMPLES:
TEMPERATURE, pH, CHLORINE DEMAND,
AND IRON AND MANGANESE CONCENTRATIONS

Temperature, pH, Chlorine Demand, and Iron and Manganese
Concentrations of Raw Water Samples (66 observations)

Temperature

mean = 14.1°C

standard deviation = 1.05°C

pH

mean = 6.75

standard deviation = 0.15

Chlorine Demand

mean = 6.00 mg/l

standard deviation = 0.35 mg/l

Iron

Total:

mean = 3.9 mg/l

standard deviation = 1.6 mg/l

Soluble:

mean = 2.6 mg/l

standard deviation = 0.7 mg/l

Manganese

Total:

mean = 2.3 mg/l

standard deviation = 0.3 mg/l

Soluble:

mean = 2.3 mg/l

standard deviation = 0.2 mg/l

APPENDIX E
HYDROGEN ION CONCENTRATIONS:
RESULTS AND STATISTICAL ANALYSES

Table E1. Hydrogen Ion Concentrations in CC-2 Effluent (H^+ x 10^{10})

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	1122	891	794	447	631
		1413	1122	891	1000	708
		1259	631	708	447	316
		<u>1265</u>	<u>881</u>	<u>798</u>	<u>631</u>	<u>552</u>
	2	1122	891	794	794	447
		794	1000	1259	794	501
		1995	1995	1585	1778	708
		<u>1304</u>	<u>1295</u>	<u>1213</u>	<u>1122</u>	<u>552</u>
	4	891	891	1000	708	501
		2512	1000	891	1122	724
		2818	1259	1778	1995	1122
		<u>2074</u>	<u>1050</u>	<u>1223</u>	<u>1275</u>	<u>782</u>
	8			1585		631
				1778		708
				1413		1413
				<u>1592</u>		<u>917</u>
	12	1st rep			891	562
		2nd rep			1413	891
		3rd rep			1585	1259
		mean			<u>1296</u>	<u>904</u>

Table E2. Analysis of Variance of CC-2 Effluent Hydrogen Ion Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	2143358.1	4	535839.5	2.71 *
Time	4366647.9	4	1091662.0	5.52 **
Interaction	1676270.4	13	128943.9	0.65
Error	8704376.0	44	197826.7	
Total	16403460.7	65		

* significant at the 5 per cent level

** significant at the 1 per cent level

Table E3. Hydrogen Ion Concentrations in Filter Effluent ($H^+ \times 10^{10}$)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)		398	398	447	447	562
		891	794	562	794	708
		1000	708	794	562	562
		<u>763</u>	<u>533</u>	<u>601</u>	<u>601</u>	<u>611</u>
		708	562	631	562	447
		1259	708	794	631	562
		1259	1122	1000	1000	631
		<u>1075</u>	<u>797</u>	<u>808</u>	<u>731</u>	<u>547</u>
		562	708	562	631	447
		1122	1122	794	794	794
		1585	1122	1000	1000	1259
		<u>1090</u>	<u>984</u>	<u>785</u>	<u>808</u>	<u>833</u>
			1259	562	562	562
			1000	562	1122	794
			1778	708	1000	1122
			<u>1346</u>	<u>611</u>	<u>895</u>	<u>826</u>
		1st rep		562	447	398
		2nd rep		1122	891	891
		3rd rep		1122	1000	1122
		mean		<u>935</u>	<u>779</u>	<u>304</u>

Table E4. Analysis of Variance of Filter Effluent Hydrogen Ion Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	933080.5	4	233270.1	2.98 *
Time	883384.7	4	220846.2	2.82 *
Interaction	715644.2	13	55049.6	0.70
Error	3449108.7	44	78386.8	
Total	5750141.0	65		

* significant at the 5 per cent level

APPENDIX F
IRON AND MANGANESE:
RESULTS AND STATISTICAL ANALYSES

Table F1. Soluble Iron in CC-2 Effluent (mg/l)


		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	1.80 2.40 0.98 <u>1.73</u>	1.80 2.10 0.80 <u>1.57</u>	0.94 1.60 0.67 <u>1.07</u>	1.10 1.00 0.47 <u>0.56</u>	0.55 0.35 0.14 <u>0.35</u>
	2	0.02 0.38 0.29 <u>0.23</u>	0.02 0.02 0.04 <u>0.03</u>	0.01 0.05 0.02 <u>0.03</u>	0.02 0.05 0.02 <u>0.03</u>	0.02 0.07 0.03 <u>0.04</u>
	4	0.01 0.03 0.03 <u>0.02</u>	0.02 0.03 0.02 <u>0.02</u>	0.02 0.03 0.06 <u>0.04</u>	0.02 0.01 0.02 <u>0.02</u>	0.02 0.08 0.02 <u>0.04</u>
	8			0.03 0.03 0.02 <u>0.03</u>	0.02 0.03 0.02 <u>0.02</u>	0.01 0.03 0.01 <u>0.02</u>
	12			0.04 0.03 0.10 <u>0.06</u>	0.03 0.03 0.03 <u>0.03</u>	0.04 0.04 0.01 <u>0.03</u>

Table F2. Analysis of Variance of CC-2 Effluent Soluble Iron Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F	
Dosage	12.4540	4	3.1135	49.01	**
Time	1.2639	4	0.3160	4.97	**
Interaction	2.5461	13	0.1959	3.08	**
Error	2.7950	44	0.0635		
Total	19.9488	65			

** significant at the 1 per cent level

Table F3. Soluble Manganese in CC-2 Effluent (mg/l)

		DETECTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	1.90	2.00	2.10	2.20	2.10
		2.10	2.10	2.10	2.00	2.00
		2.40	2.30	2.40	2.70	2.40
		<u>2.10</u>	<u>2.10</u>	<u>2.20</u>	<u>2.30</u>	<u>2.20</u>
	2	1.70	1.60	2.00	0.52	1.20
		2.30	2.10	1.20	1.60	1.10
		2.40	1.80	1.60	2.40	1.50
		<u>2.10</u>	<u>1.80</u>	<u>1.60</u>	<u>1.50</u>	<u>1.30</u>
	4	0.05	0.01	0.01	0.04	0.02
		0.59	1.50	0.05	0.23	0.03
		0.02	1.50	0.36	0.01	0.01
		<u>0.22</u>	<u>1.00</u>	<u>0.14</u>	<u>0.09</u>	<u>0.02</u>
	8		0.12	0.16	0.11	0.11
			0.17	0.13	0.05	0.05
			0.11	0.09	0.06	0.05
			<u>0.13</u>	<u>0.13</u>	<u>0.07</u>	<u>0.07</u>
	12			0.19	0.18	0.14
				0.19	0.17	0.13
				0.21	0.18	0.13
				<u>0.20</u>	<u>0.18</u>	<u>0.13</u>

Table F4. Analysis of Variance of CC-2 Effluent Soluble Manganese Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F	
Dosage	47.3619	4	11.3405	104.67	**
Time	1.1439	4	0.2860	2.53	
Interaction	2.1798	13	0.1677	1.48	
Error	4.9776	44	0.1131		
Total	59.4686	65			

** significant at the 1 per cent level

Table F5. Soluble Iron in Filter Effluent (mg/l)



		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	0.02	0.02	0.03	0.03	0.04
		0.02	0.04	0.02	0.02	0.03
		0.02	0.02	0.03	0.02	0.02
		<u>0.02</u>	<u>0.03</u>	<u>0.03</u>	<u>0.02</u>	<u>0.03</u>
	2	0.01	0.05	0.02	0.05	0.02
		0.08	0.02	0.05	0.04	0.02
		0.02	0.02	0.02	0.02	0.02
		<u>0.04</u>	<u>0.03</u>	<u>0.03</u>	<u>0.04</u>	<u>0.02</u>
	4	0.03	0.04	0.01	0.01	0.03
		0.04	0.02	0.02	0.02	0.06
		0.02	0.02	0.01	0.04	0.02
		<u>0.03</u>	<u>0.03</u>	<u>0.01</u>	<u>0.02</u>	<u>0.04</u>
	8		0.03	0.02	0.03	0.02
			0.03	0.03	0.03	0.02
			0.02	0.04	0.05	0.01
			<u>0.03</u>	<u>0.03</u>	<u>0.04</u>	<u>0.02</u>
	12		0.05	0.01	0.06	0.06
			0.03	0.03	0.02	0.02
			0.02	0.02	0.01	0.01
			<u>0.03</u>	<u>0.02</u>	<u>0.03</u>	<u>0.03</u>

Table F6. Analysis of Variance of Filter Effluent Soluble Iron Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	0.00026111	4	0.0000653	0.30
Time	0.00004778	4	0.0000119	0.05
Interaction	0.00249278	13	0.0001917	0.37
Error	0.00966667	44	0.0002197	
Total	0.01246212	65		

Table F7. Total Iron in Filter Effluent (mg/l)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	0.14	0.13	0.10	0.34	0.14
		0.04	0.04	0.11	0.08	0.13
		0.03	0.03	0.03	0.05	0.06
		0.07	0.07	0.08	0.16	0.11
	2	0.10	0.14	0.06	0.05	0.05
		0.05	0.04	0.05	0.06	0.07
		0.14	0.02	0.03	0.05	0.02
		0.10	0.07	0.05	0.05	0.05
	4	0.03	0.06	0.02	0.04	0.03
		0.02	0.04	0.05	0.07	0.09
		0.02	0.02	0.04	0.03	0.07
		0.02	0.04	0.04	0.05	0.06
	8		0.03	0.02	0.06	0.02
			0.03	0.03	0.03	0.04
			0.02	0.02	0.09	0.05
			0.03	0.02	0.06	0.04
	12	1st rep 2nd rep 3rd rep mean		0.05	0.02	0.08
				0.04	0.02	0.02
				0.02	0.02	0.02
				0.04	0.02	0.04

Table F8. Analysis of Variance of Filter Effluent Total Iron Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	0.03863	4	0.00966	4.45
Time	0.00571	4	0.00143	0.66
Interaction	0.02233	13	0.00172	0.79
Error	0.09540	54	0.00217	
Total	0.16127	65		

* significant at the 1 per cent level

Table F9. Soluble Manganese in Filter Effluent (mg/l)



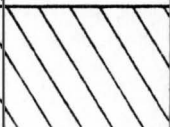
		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	0.19	0.15	0.24	0.24	0.60
		0.30	0.19	0.19	0.14	0.11
		0.09	0.17	0.29	0.37	0.45
		<u>0.19</u>	<u>0.17</u>	<u>0.24</u>	<u>0.25</u>	<u>0.39</u>
	2	0.70	0.56	0.47	0.48	0.49
		0.02	0.11	0.01	0.01	0.01
		0.07	0.02	0.02	0.08	0.19
		<u>0.26</u>	<u>0.23</u>	<u>0.17</u>	<u>0.19</u>	<u>0.23</u>
	4	0.44	0.43	0.61	0.52	0.39
		0.02	0.03	0.02	0.15	0.07
		0.06	0.04	0.02	0.02	0.02
		<u>0.17</u>	<u>0.17</u>	<u>0.22</u>	<u>0.23</u>	<u>0.16</u>
	8		0.02	0.41	0.33	0.35
			0.02	0.02	0.02	0.03
			0.04	0.02	0.03	0.02
			<u>0.03</u>	<u>0.15</u>	<u>0.13</u>	<u>0.13</u>
12			0.29	0.33	0.30	
			0.02	0.02	0.01	
			0.03	0.05	0.02	
			<u>0.11</u>	<u>0.13</u>	<u>0.11</u>	

Table F10. Analysis of Variance of Filter Effluent Soluble Manganese Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	0.19136	4	0.04784	1.02
Time	0.03686	4	0.00922	0.20
Interaction	0.10662	13	0.00820	0.17
Error	2.07200	44	0.04709	
Total	2.39804	65		

Table F11. Total Manganese in Filter Effluent (mg/l)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	0.19	0.15	0.24	0.25	0.61
		0.30	0.18	0.19	0.13	0.11
		0.08	0.16	0.28	0.37	0.45
		<u>0.19</u>	<u>0.16</u>	<u>0.24</u>	<u>0.25</u>	<u>0.39</u>
	2	0.70	0.57	0.47	0.50	0.50
		0.01	0.10	0.01	0.01	0.07
		0.06	0.02	0.02	0.08	0.18
		<u>0.26</u>	<u>0.23</u>	<u>0.17</u>	<u>0.20</u>	<u>0.25</u>
	4	0.44	0.48	0.61	0.53	0.41
		0.02	0.02	0.03	0.15	0.09
		0.06	0.03	0.06	0.02	0.02
		<u>0.17</u>	<u>0.18</u>	<u>0.23</u>	<u>0.23</u>	<u>0.17</u>
	8		0.02	0.39	0.34	0.36
			0.05	0.07	0.02	0.04
			0.03	0.02	0.03	0.05
			<u>0.03</u>	<u>0.16</u>	<u>0.13</u>	<u>0.15</u>
	12	1st rep 2nd rep 3rd rep mean		0.30	0.34	0.30
				0.02	0.02	0.02
				0.03	0.03	0.02
				<u>0.12</u>	<u>0.13</u>	<u>0.11</u>

Table F12. Analysis of Variance of Filter Effluent Total Manganese Concentrations

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	0.18357	4	0.04589	0.96
Time	0.04773	4	0.01193	0.25
Interaction	0.10517	13	0.00809	0.17
Error	2.10707	44	0.04789	
Total	2.42710	65		

Table F13. Iron and Manganese Concentrations in Filter Influent as a Function of Time (mg/l)

		Total Iron	Total Manganese	Soluble Iron	Soluble Manganese
HOURS SINCE FILTER BACKWASH	.25	4.2	2.3	0.03	0.19
	4	5.0	2.4	0.02	0.17
	8	4.4	2.3	0.02	0.19
	12	3.2	2.4	0.01	0.17
	16	2.9	2.4	0.01	0.19
	20	2.4	2.5	0.04	0.20
	24	2.6	2.6	0.02	0.17
	28	2.7	2.5	0.02	0.21
	32	2.7	2.4	0.02	0.21

Table F14. Iron and Manganese Concentrations in Pilot Plant Effluent as a Function of Time (mg/l)

		Total Iron	Total Manganese	Soluble Iron	Soluble Manganese
HOURS SINCE FILTER BACKWASH	.25	0.05	0.03	0.01	0.01
	4	0.03	0.02	0.02	0.01
	8	0.02	0.02	0.01	0.01
	12	0.02	0.02	0.01	0.02
	16	0.02	0.02	0.02	0.02
	20	0.03	0.02	0.02	0.01
	24	0.05	0.03	0.01	0.01
	28	0.23	0.16	0.02	0.01
	32	2.0	1.4	0.02	0.01

Table F15. Iron Removal Profiles Through Filter Medium

		Total Iron Concentration (mg/l)			Soluble Iron Concentration (mg/l)		
Hours Since Filter Backwash		0.25	16	32	0.25	16	32
Depth in Filter Medium (cm)	7.6	0.44	3.7	5.0	0.02	0.02	0.02
	15.2	0.16	3.3	3.5	0.12	0.03	0.02
	22.9	0.10	3.0	3.6	0.03	0.02	0.02
	30.5	0.10	2.6	1.8	0.02	0.02	0.02
	38.1	0.06	1.6	2.0	0.02	0.03	0.02
	45.7	0.05	0.79	3.3	0.02	0.03	0.02
	53.3	0.04	0.13	3.4	0.01	0.01	0.01
	61.0	0.03	0.07	2.1	0.02	0.02	0.01
	68.6	0.04	0.02	2.0	0.01	0.01	0.03
	Filter Effluent	0.05	0.02	2.0	0.01	0.02	0.02

Table F16. Manganese Removal Profile Through Filter Medium

		Total Manganese Concentration (mg/l)			Soluble Manganese Concentration (mg/l)		
Hours Since Filter Backwash		0.25	16	32	0.25	16	32
	7.6	0.35	4.0	4.6	0.01	0.15	0.18
	15.2	0.18	1.9	2.5	0.01	0.08	0.16
	22.9	0.10	1.7	2.7	0.01	0.02	0.11
	30.5	0.07	1.2	2.2	0.02	0.00	0.05
	38.1	0.05	0.77	1.6	0.02	0.00	0.01
	45.7	0.05	0.41	2.4	0.02	0.01	0.00
	53.3	0.04	0.06	2.5	0.01	0.03	0.01
	61.0	0.04	0.05	1.5	0.01	0.01	0.01
	68.6	0.03	0.02	1.5	0.01	0.01	0.01
	Filter Effluent	0.03	0.02	1.4	0.01	0.02	0.01

APPENDIX G
FILTER HEAD LOSS: RESULTS

Table G1. Head Loss Through Filter Medium (cm)

		Hours Since Filter Backwash								
		0.25	4	8	12	16	20	24	28	32
Depth in Filter Medium (cm)	7.6	2.5	8.9	22.1	31.0	37.6	40.9	45.7	50.0	53.8
	15.2	4.3	11.4	26.7	33.5	43.7	53.8	64.0	68.1	79.2
	22.9	4.8	12.4	29.7	41.7	52.6	65.8	73.4	79.2	91.9
	30.5	6.1	13.7	31.0	42.5	54.1	68.6	78.5	87.6	99.1
	38.1	6.6	14.7	31.8	43.7	55.4	70.4	80.3	91.9	102.9
	45.7	7.4	15.7	32.8	44.7	56.6	71.6	81.8	93.2	104.9
	53.3	8.1	16.8	33.5	45.7	57.7	72.8	82.8	94.7	106.7
	61.0	8.9	17.8	33.8	46.7	58.4	73.7	84.1	96.0	108.0
	68.6	9.4	18.3	34.5	47.2	58.9	74.2	84.6	96.5	108.7
	Total	9.6	18.5	34.8	47.5	59.2	74.4	84.8	96.7	109.2

APPENDIX H
CHLORINE DEMAND:
RESULTS AND STATISTICAL ANALYSES

Table H1. Chlorine Demand of Pilot Plant Effluent (mg/l)

		DETENTION TIME (minutes)				
		5	10	15	20	30
APPLIED OZONE DOSAGE (mg/l)	0	4.4	5.1	4.0	3.9	4.1
		4.4	3.6	3.8	4.6	4.6
		5.0	4.4	5.0	4.9	4.9
		<u>4.6</u>	<u>4.4</u>	<u>4.3</u>	<u>4.5</u>	<u>4.5</u>
	2	4.6	3.7	4.2	4.1	4.2
		4.4	3.0	4.0	3.4	3.8
		4.0	4.8	4.6	4.1	4.0
		<u>4.3</u>	<u>3.8</u>	<u>4.3</u>	<u>3.9</u>	<u>4.0</u>
	4	4.0	4.0	3.7	4.1	2.8
		3.5	4.3	4.2	3.5	3.6
		4.9	3.8	4.2	4.8	4.0
		<u>4.1</u>	<u>4.0</u>	<u>4.0</u>	<u>4.1</u>	<u>3.5</u>
	8		3.8	3.8	3.7	4.0
			4.0	3.8	4.2	4.2
			3.9	3.8	3.6	4.2
			<u>3.9</u>	<u>3.8</u>	<u>3.8</u>	<u>4.1</u>
	12			4.6	3.6	3.7
				3.7	4.2	3.8
				4.5	4.0	4.4
				<u>4.3</u>	<u>3.9</u>	<u>4.0</u>

Table H2. Analysis of Variance of Pilot Plant Effluent Chlorine Demand

Source of Error	Sum of Squares	Degrees of Freedom	Mean Square	Computed F
Dosage	2.33235	4	0.58309	2.68 *
Time	0.53885	4	0.13471	0.62
Interaction	1.67521	13	0.12886	0.59
Error	9.58667	44	0.21789	
Total	14.37939	65		

* significant at the 5 per cent level

APPENDIX I
DESCRIPTION OF THE TREATMENT PROCESS AT
THE SIOUX FALLS WATER TREATMENT PLANT

DESCRIPTION OF THE TREATMENT PROCESS
AT THE SIOUX FALLS WATER TREATMENT PLANT

The city of Sioux Falls, South Dakota obtains its water supply from the Big Sioux aquifer below and adjacent to the Big Sioux River north of Sioux Falls. While there are two surface supply intakes on the diversion canal, the city depends on a field of 34 wells to provide the water needed. The treatment plant is designed primarily to remove iron and manganese and partially soften the water.

A flow diagram of the treatment plant is presented in Figure 11. Upon entering the plant, the water receives an injection of chlorine, minimizing the possibility of bacteria passing through the filter bed. Following prechlorination, the water enters solids contact basins where slaked lime (Ca(OH)_2) and a polymer is added. Lime removes iron and manganese and also precipitates hardness. The polymer is added to improve flocculation. Next, the clarified effluent from the solids contact basins flows to a recarbonation basin where carbon dioxide (CO_2) is added to adjust the alkalinity to prevent a buildup of calcium carbonate (CaCO_3) on the grains of the filter media. In addition, phosphate is added to help stabilize the water.

Prior to filtration, the water is chlorinated to kill unwanted bacteria and fluoridated to aid in the prevention of tooth decay. The rapid gravity filters have a media consisting of anthracite or a combination of anthracite and sand or gravel or both. The filtration

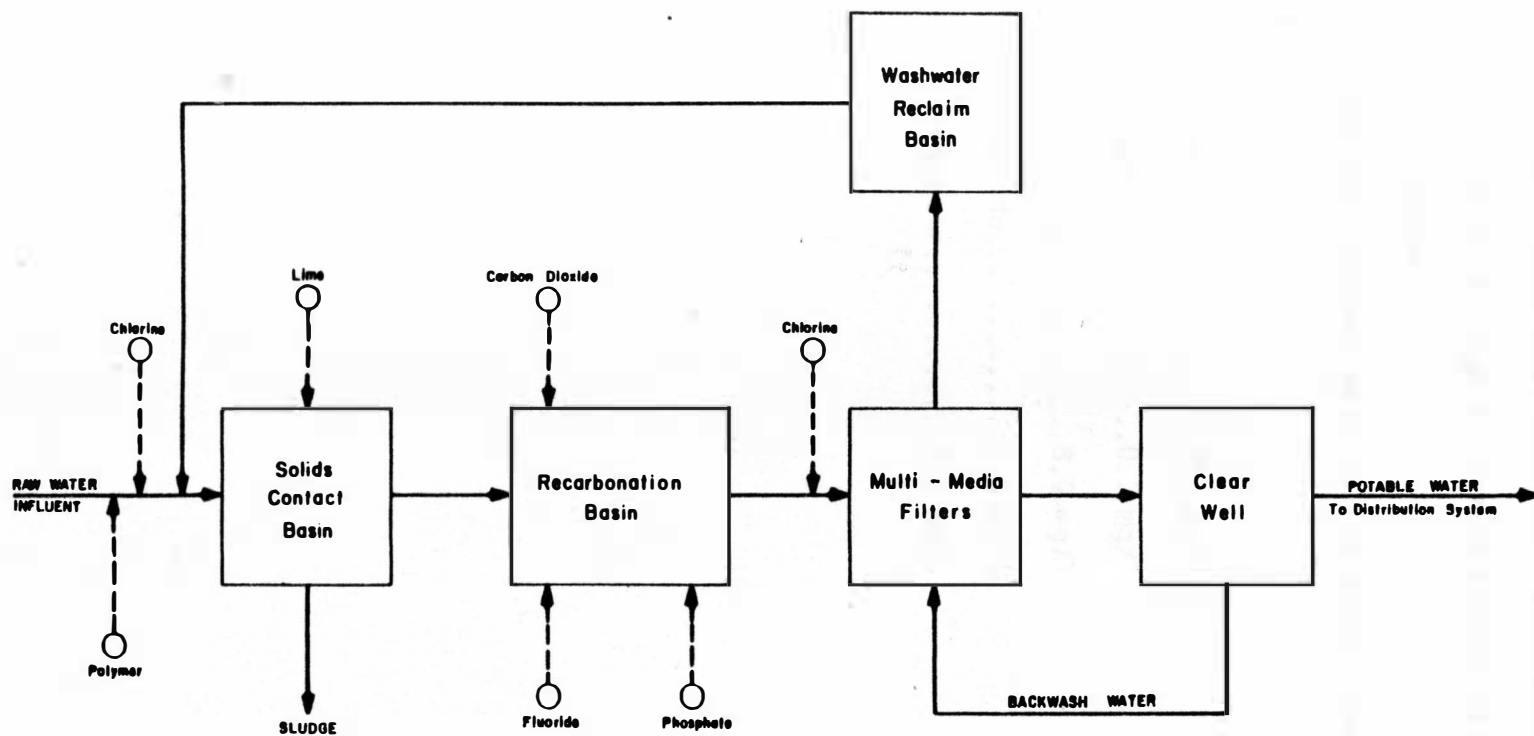


Figure I1. Sioux Falls Water Treatment Plant Flow Diagram

process screens out any remaining suspended impurities. The final purified water is stored in a large clearwell before being pumped out into the distribution system.

The usual chemical dosages used in the water treatment process are as follows:

Lime.....	300 mg/l
Polymer.....	0.1 mg/l
Chlorine.....	8.5 mg/l
Fluoride.....	1.5 mg/l
Phosphate.....	1.0 mg/l

APPENDIX J
OZONATION COST CALCULATIONS

ESTIMATING THE COST OF OZONATION IN WATER TREATMENT

Assumptions: Treatment Plant Design Capacity = 52 MGD

Applied Ozone Dosage: 4 - 8 mg/l

Detention time in contact chamber = 5 minutes

$$\begin{aligned}
 \text{Required Ozone Generation Capacity} &= (8.34)(\text{MGD})(\text{mg/l}) \\
 &= (8.34)(52)(8) \\
 &= 3469 \text{ lb/day} \\
 &= 1574 \text{ kg/day}
 \end{aligned}$$

$$\begin{aligned}
 \text{Required Contact Chamber Volume} &= \frac{(52,000,000 \text{ gal/day})(5 \text{ min})}{(7.481 \text{ gal/ft}^3)(1440 \text{ min/day})} \\
 &= 24,135 \text{ ft}^3 \\
 &= 684 \text{ m}^3
 \end{aligned}$$

Table J1. Computation of Cost-Updating Indices

Cost Component	Cost Index	Oct. 1978 Value of Index	April 1981 Value of Index	April 1981 Value Oct. 1978 Value
Excavation and Sitework	ENR Wage Index for Skilled Labor	247.0	292.0	1.18
Manufactured Equipment	BLS General Purpose Machinery & Equipment	221.3	283.5	1.28
Concrete	BLS Concrete Ingredi- ents	221.1	289.5	1.31
Steel	BLS Steel Mill Products	262.1	330.6	1.26
Labor	ENR Wage Index for Skilled Labor	247.0	292.0	1.18
Housing	ENR Building Cost Index	254.8	305.5	1.20
Maintenance Materials	BLS Producer Price In- dex for Finished Goods	199.7	267.7	1.34

Table J2. Computation of Costs of Ozonation

		Cost Component	Cost as of October 1978 (dollars)	Updating Index	Cost as of April 1981 (dollars)
Construction Costs	Generation System	Manufactured Equipment	1,615,980	1.28	2,066,450
		Concrete	2,380	1.31	3,120
		Steel	2,440	1.26	3,070
		Labor	286,200	1.18	337,720
		Housing	44,770	1.20	53,720
		Subtotal	1,951,770	- -	2,466,080
		Miscellaneous and Contingency (15 per cent of subtotal)	292,770	- -	369,910
		TOTAL	2,244,540	- -	2,835,990
	Contact Chamber	Excavation and Sitework	2,700	1.18	3,190
		Concrete	8,750	1.31	11,460
		Steel	14,980	1.26	18,870
		Labor	20,510	1.18	24,200
		Subtotal	46,970	- -	57,720
		Miscellaneous and Contingency (15 per cent of subtotal)	7,050	- -	8,660
		TOTAL	54,020	- -	66,380
	Total Construction Cost		2,298,560	- -	2,902,370
Operation and Maintenance Costs	Maintenance Materials		31,150/yr	1.34	41,740/yr
	Electrical Energy (2,768,280 kW-hr/yr)(\$0.035/kW-hr)				96,390/yr
	Labor (2,920 hr/yr)(\$10/hr)				29,200/yr
	Total Operation and Maintenance Cost				167,330/yr

Computation of Total Annual Cost of Ozonation

$$T_a = C_a + O\&M$$

$$C_a = (CRF)(C_t)$$

$$CRF = \frac{i}{(1 + i)^n - 1} + i$$

where: T_a = total annual cost

C_a = annual repayment on construction cost

O&M = annual operation and maintenance cost

C_t = total construction cost

CRF = capital recovery factor

i = annual interest rate

n = number of years in repayment period

Computation of Cost per 3.79 m³ (1000 gallons)

$$O\&M/1000 \text{ gal} = 1000 \frac{O\&M}{(15,000,000 \text{ gal/day})(365 \text{ days/yr})}$$

Total Annual Cost per 1000 gallons =

$$1000 \frac{T_a}{(15,000,000 \text{ gal/day})(365 \text{ days/yr})}$$

where: O&M = annual operation and maintenance cost

T_a = total annual cost